

Supporting Information for:

Homo- and copolymerization of norbornene using tridentate

IzQO palladium catalysts with dimethylaminoethyl as a side arm

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1. Additional polymerization results

Table S1 Norbornene polymerization catalyzed by **3** and **4a–4d** activated by Et₂AlCl^a

entry	cat.(μ mol)	T (°C)	Al/Pd	t (min)	Conv. (%)	activity ^b
1	4a (1)	20	500	2	31.0	9.3
2	4a (1)	40	500	2	99.9	30.0
3	4a (1)	60	500	2	47.3	14.2
4	4a (1)	80	500	2	27.7	8.3
5	4a (1)	40	200	2	92.3	27.7
6	4a (1)	40	200	1	97.7	58.6
7	4a (1)	40	100	1	98.8	59.3
8	4a (0.5)	40	100	1	66.3	79.6
9	4b (0.5)	40	100	1	60.3	72.4
10	4c (0.5)	40	100	1	99.9	119.9
11	4c (0.3)	40	100	1	97.2	194.4
12	4d (0.5)	40	100	1	55.9	67.1
13	3 (0.5)	40	100	1	38.6	46.3

^aPolymerization conditions: solvent, 1,2-dichlorobenzene; V_{total} , 10 mL; norbornene, 1.0 g; Et₂AlCl, 2.0 M in hexane. ^bIn units of 10⁶ g of PNB (mol of Pd)⁻¹ h⁻¹.

Table S2 NB-UA copolymerization catalyzed by **3** and **4a–4d** activated by Et₂AlCl or MAO^a

entry	cat.	Cocat.	n (total monomer)	comonomer (mol%)	Yield (mg)
1	4c	Et ₂ AlCl	10	5	28
2	4c	Et ₂ AlCl	10	5	10
3 ^b	4c	MAO	10	5	5.6
4	4a	Et ₂ AlCl	10	5	2
5	4b	Et ₂ AlCl	10	5	trace
6	4d	Et ₂ AlCl	10	5	5.3
7	3	Et ₂ AlCl	10	5	trace

^aPolymerization conditions: [Pd], 5 μ mol; solvent, 1,2-dichlorobenzene; V_{total} , 15 mL; $n_{\text{total monomer}}$, 10 mmol; Et₂AlCl, 2.0 M in hexane, Al/Pd = 200; 40 °C, 1 h. ^bMAO instead of Et₂AlCl, MAO, 1.5 M in toluene; Al/Pd = 1000.

2. NMR spectra of the compounds 1–2 and complexes 3 and 4a–4d.

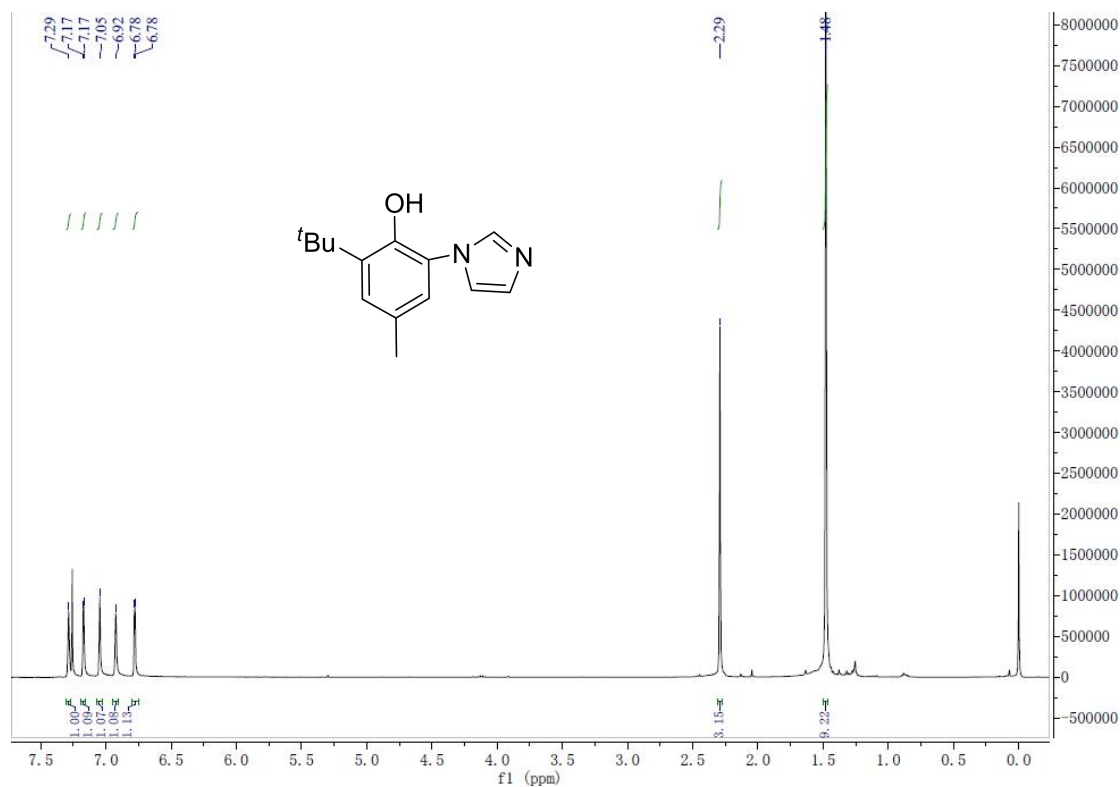


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectra of compound 1.

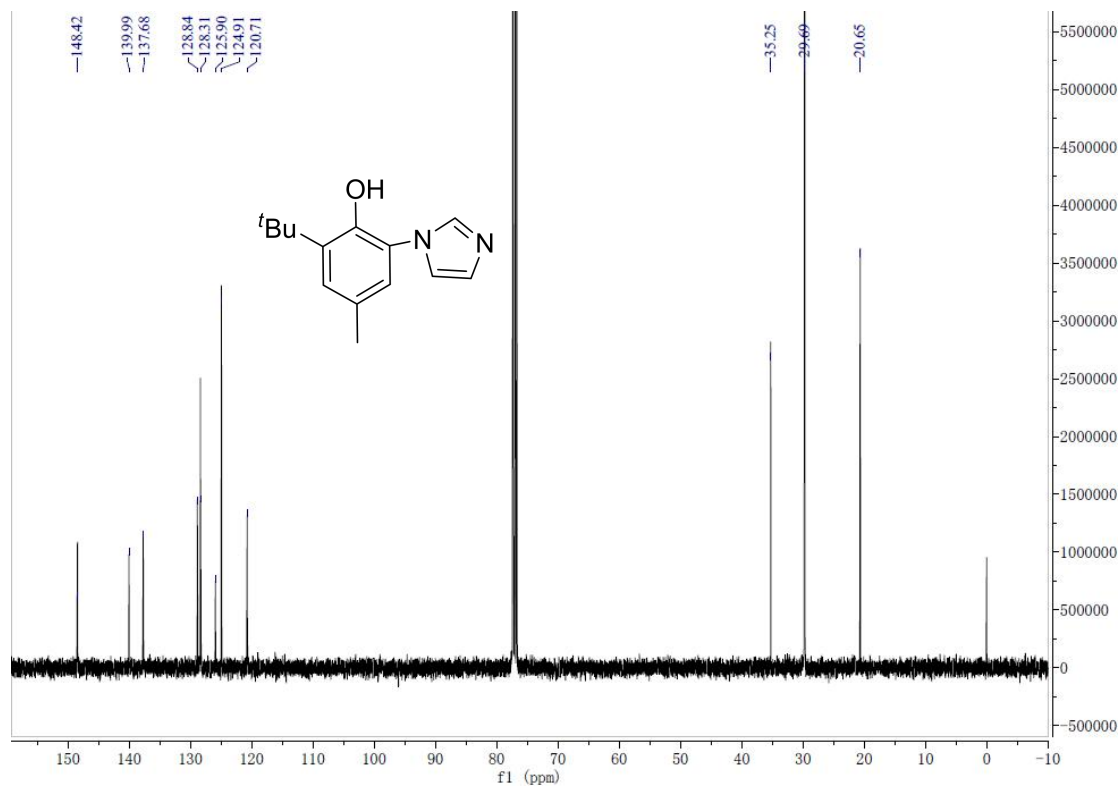


Figure S2. ¹³C NMR (101 MHz, CDCl₃) spectra of compound 1.

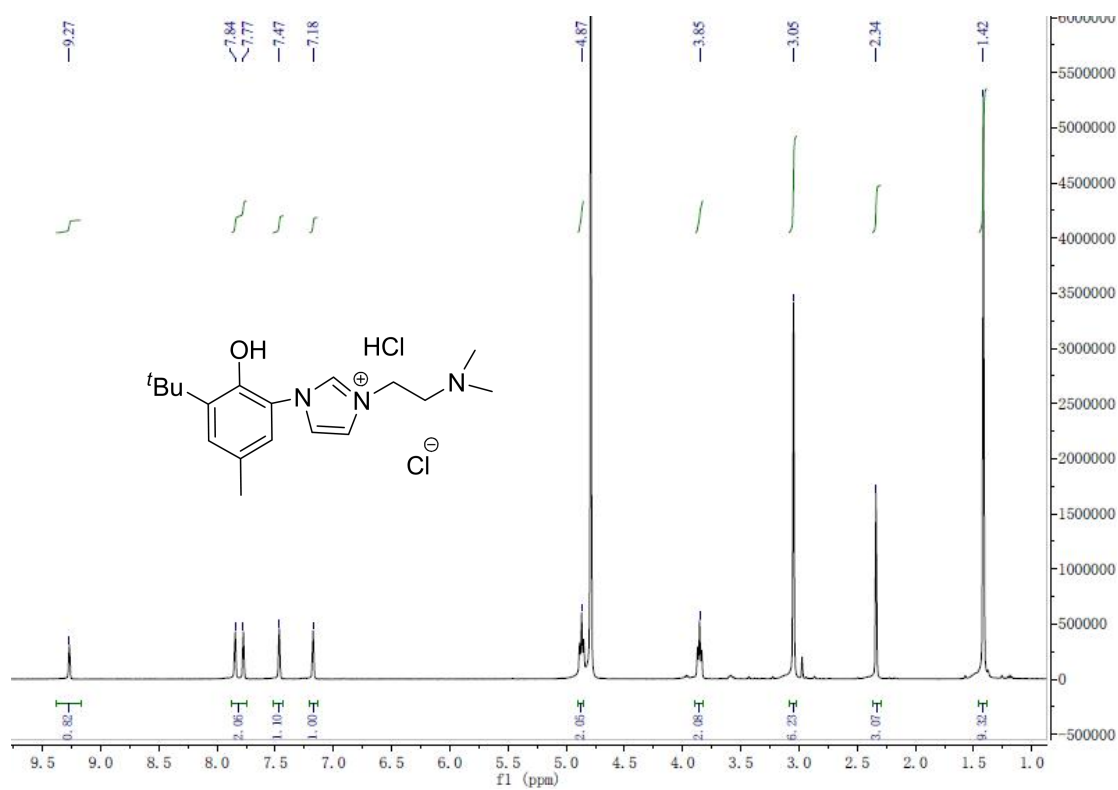


Figure S3. ^1H NMR (400 MHz, D_2O) spectra of compound 2.

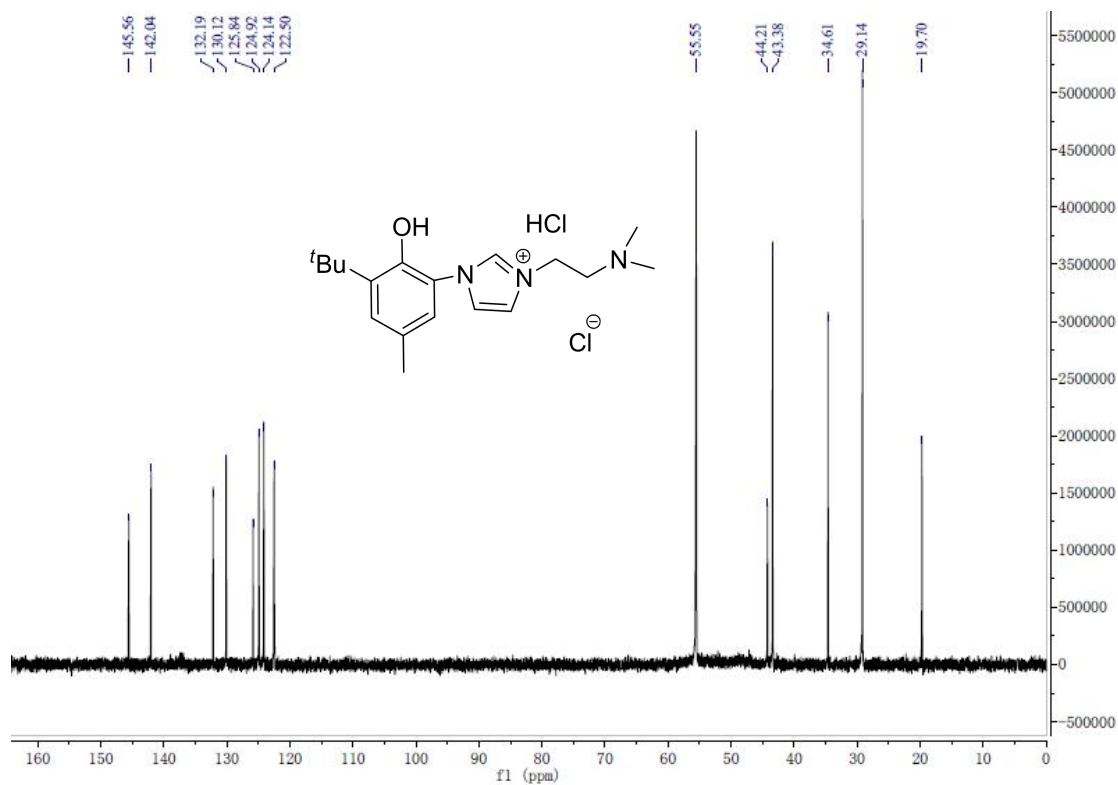


Figure S4. ^{13}C NMR (101 MHz, D_2O) spectra of compound 2.

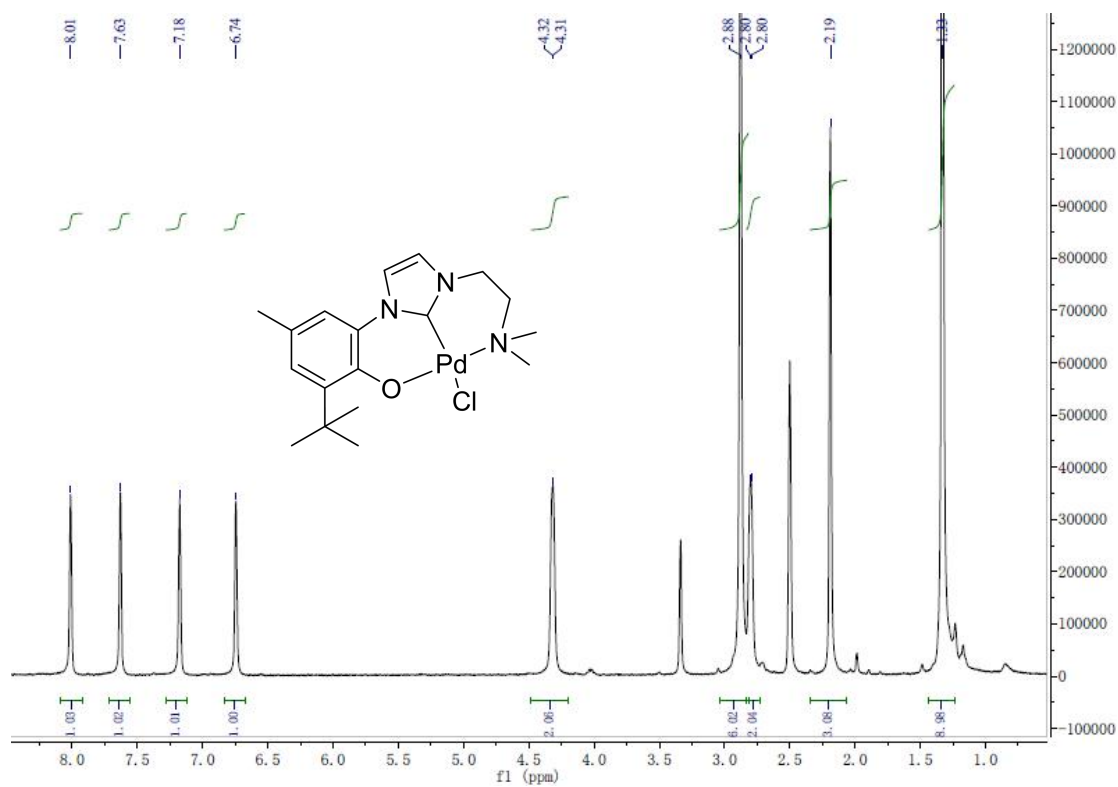


Figure S5. ^1H NMR (400 MHz, DMSO) spectra of complex 3.

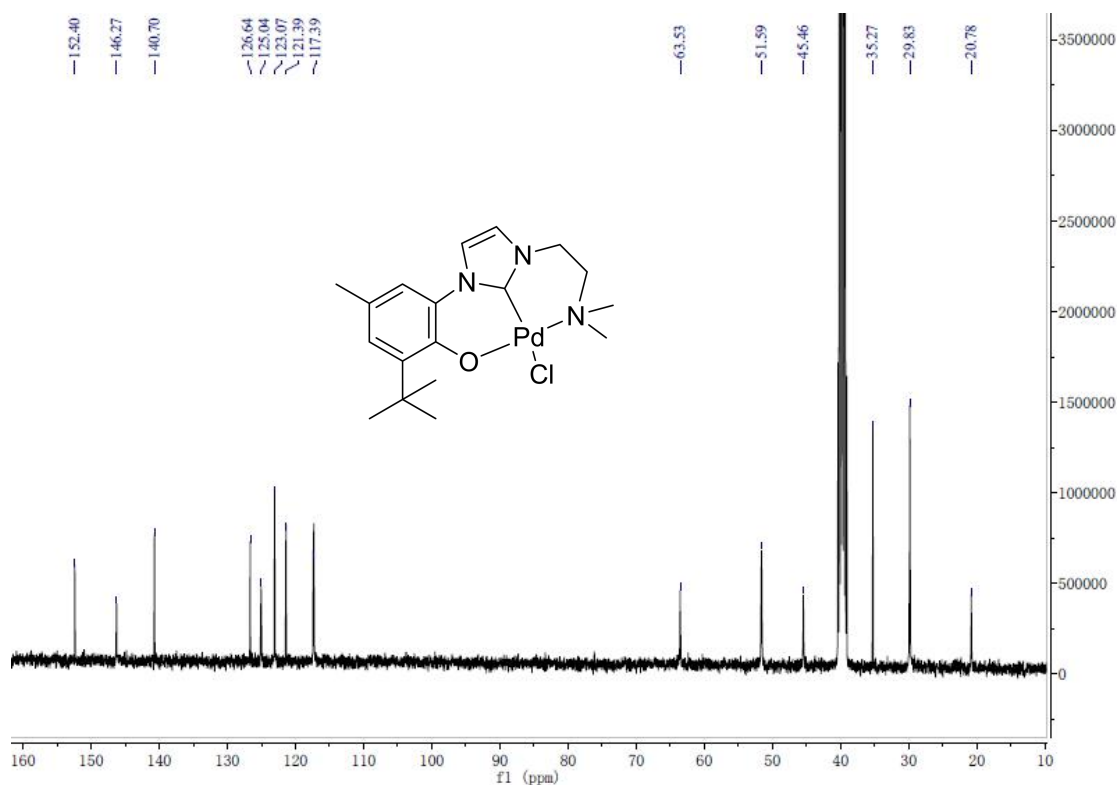


Figure S6. ^{13}C NMR (101 MHz, DMSO) spectra of complex 3.

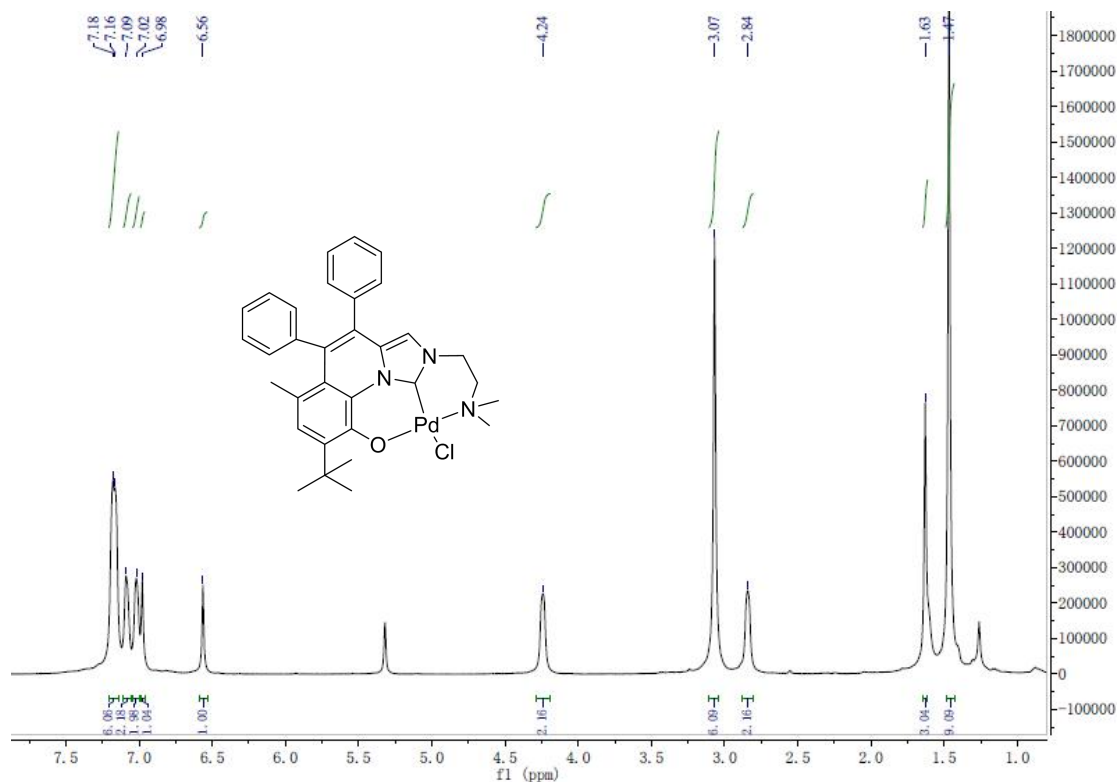


Figure S7. ¹H NMR (400 MHz, CD₂Cl₂) spectra of complex 4a.

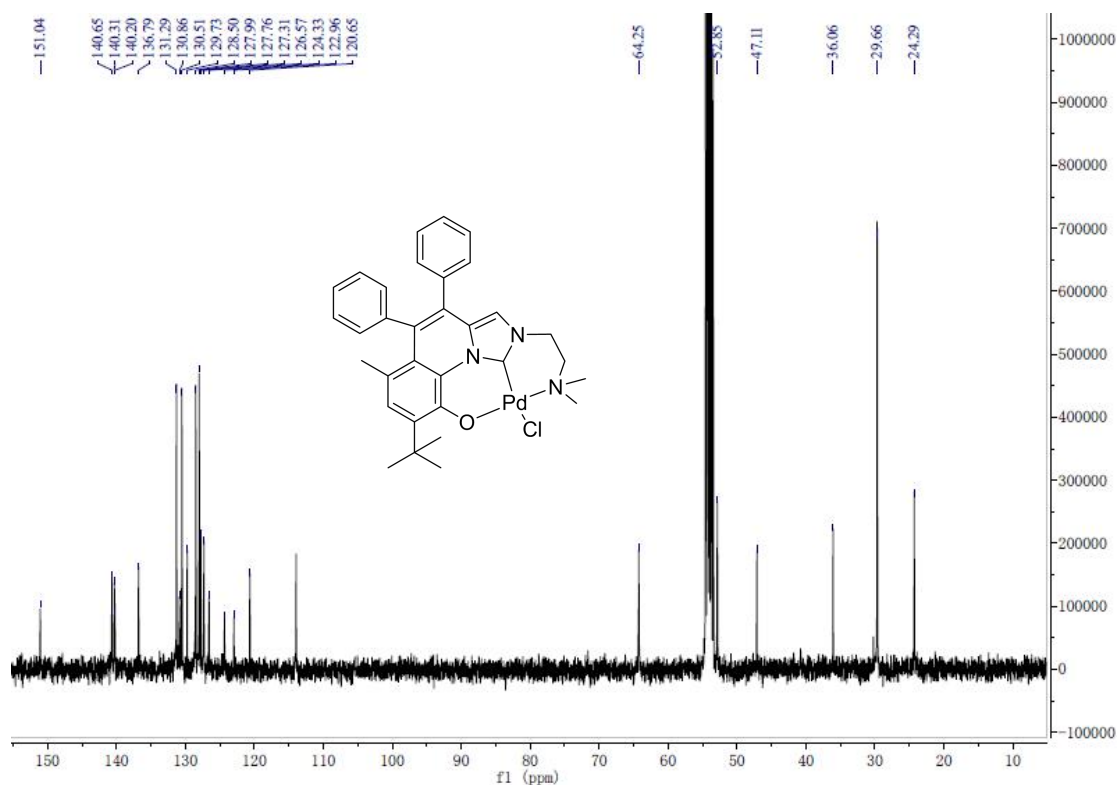


Figure S8. ¹³C NMR (101 MHz, CD₂Cl₂) spectra of complex 4a.

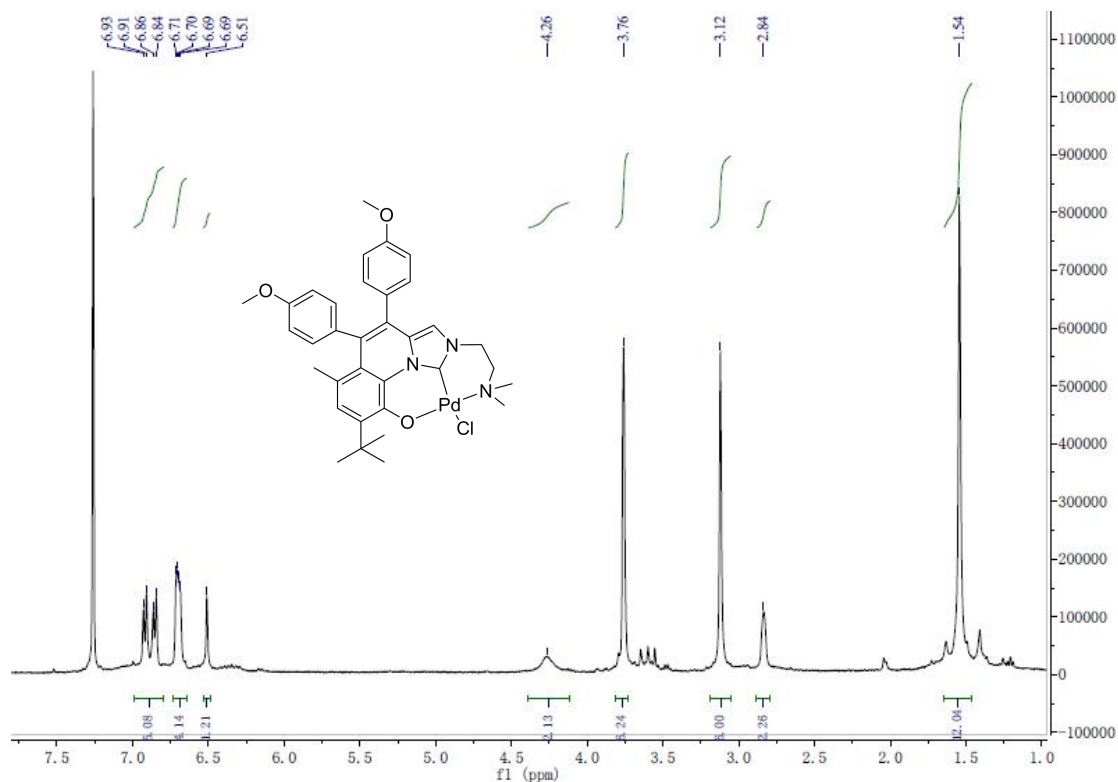


Figure S9. ^1H NMR (400 MHz, CDCl_3) spectra of complex **4b**.

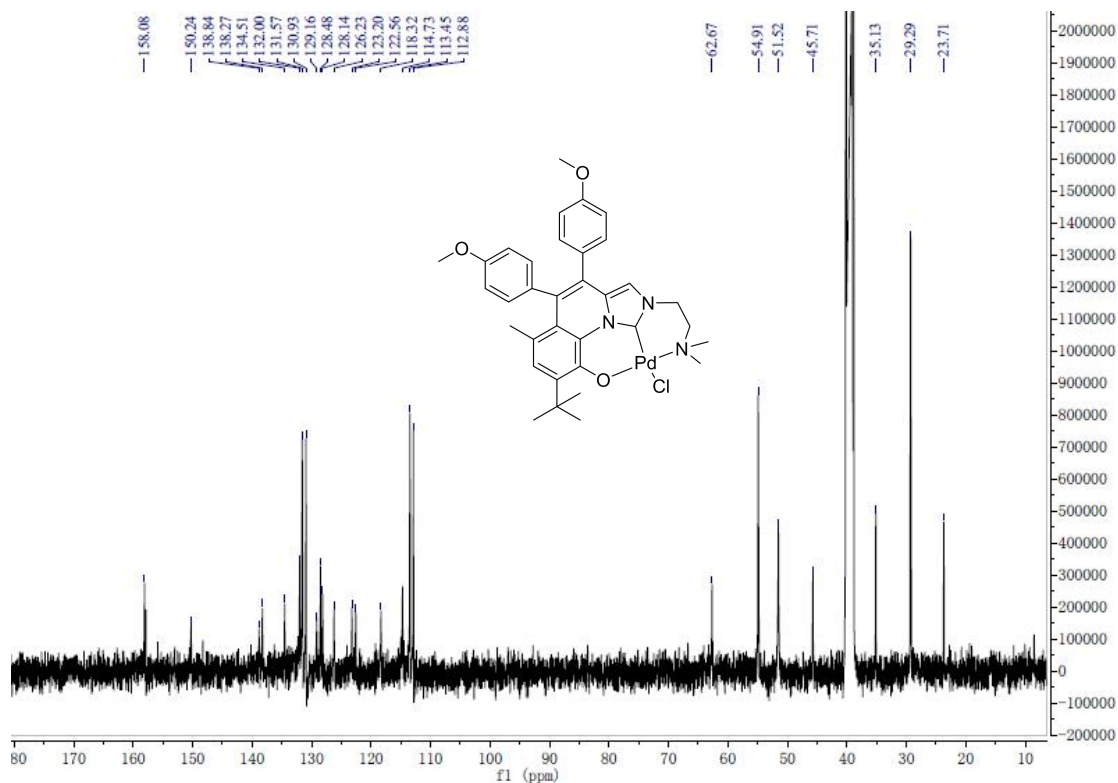
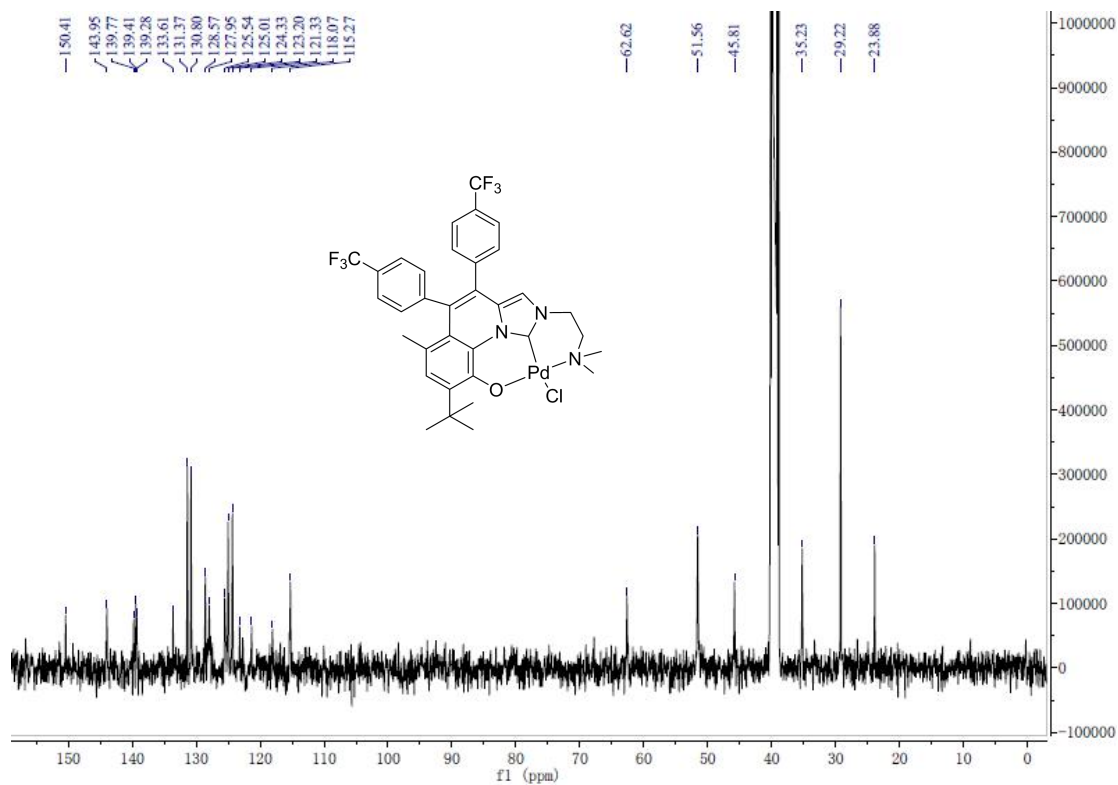
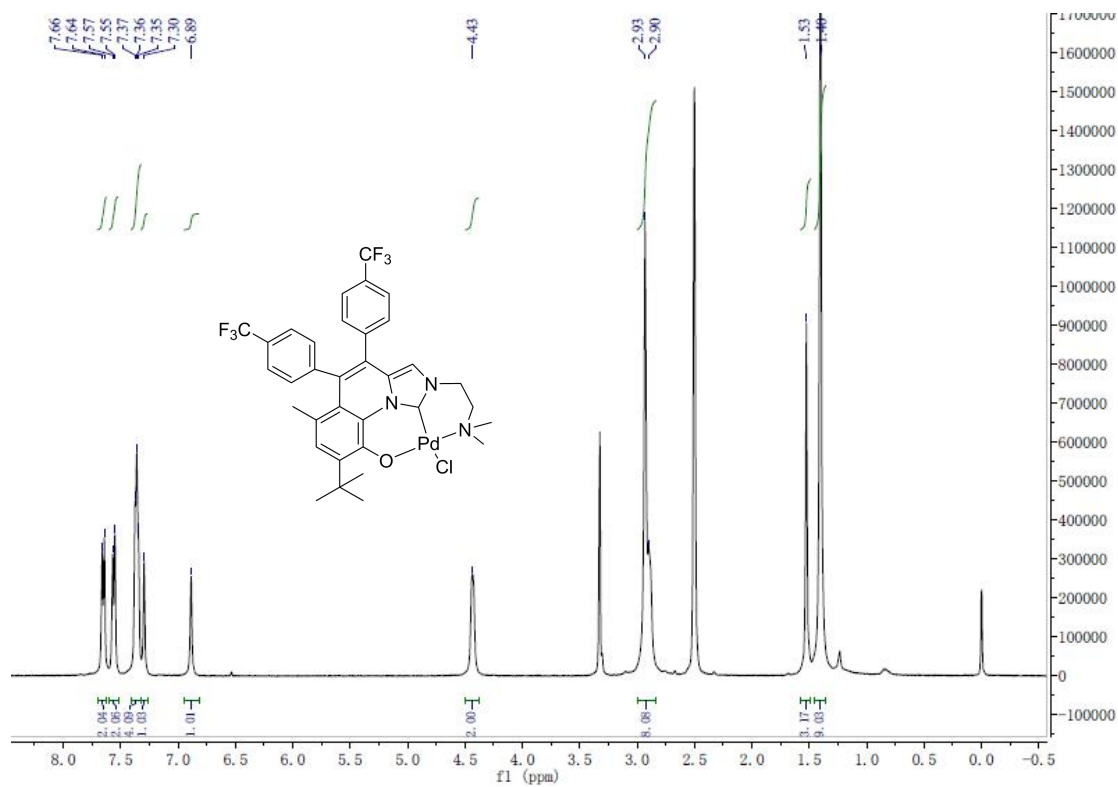


Figure S10. ^{13}C NMR (101 MHz, DMSO) spectra of complex **4b**.



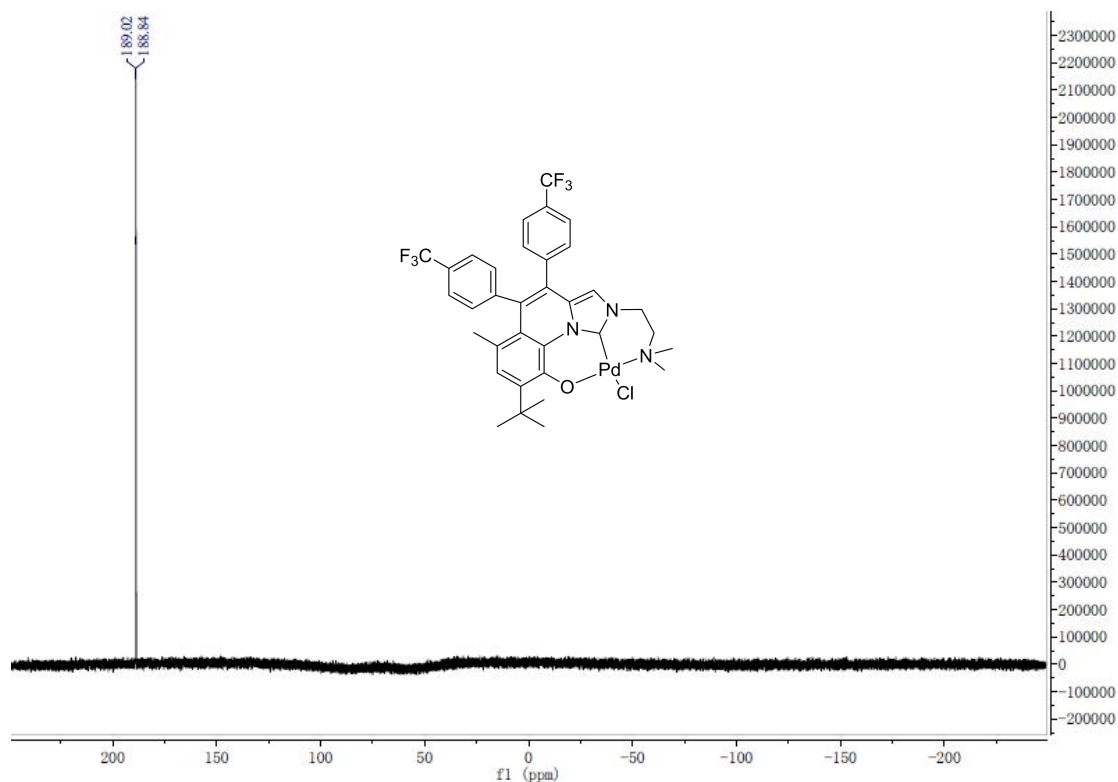


Figure S13. ^{19}F NMR (376 MHz, DMSO) spectra of complex **4c**.

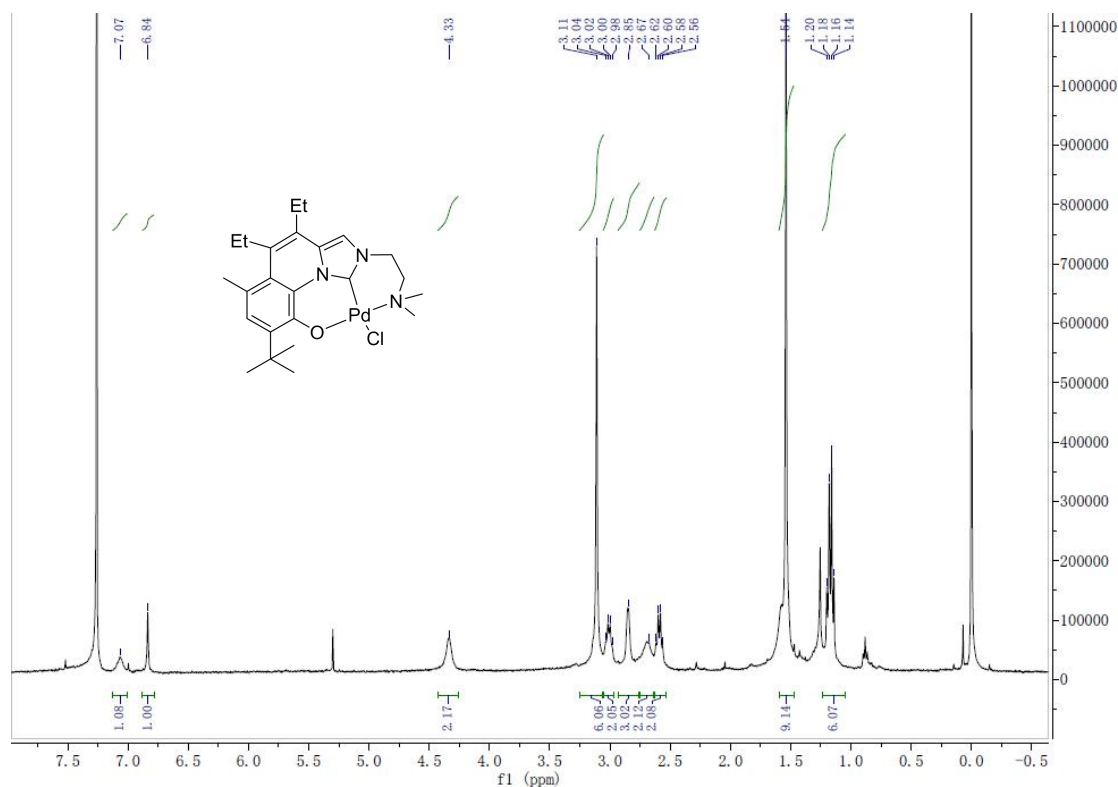


Figure S14. ^1H NMR (400 MHz, CDCl_3) spectra of complex **4d**.

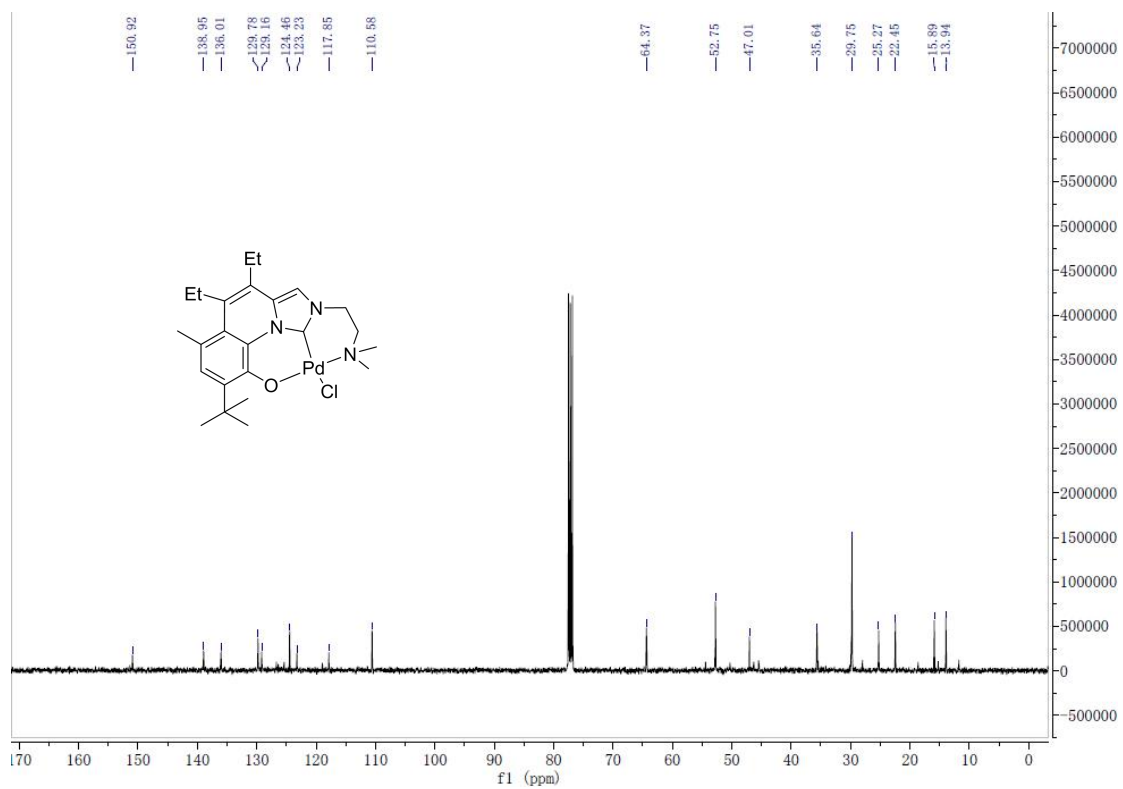


Figure S15. ^{13}C NMR (101 MHz, CDCl_3) spectra of complex **4d**.

3. NMR spectra of polymers.

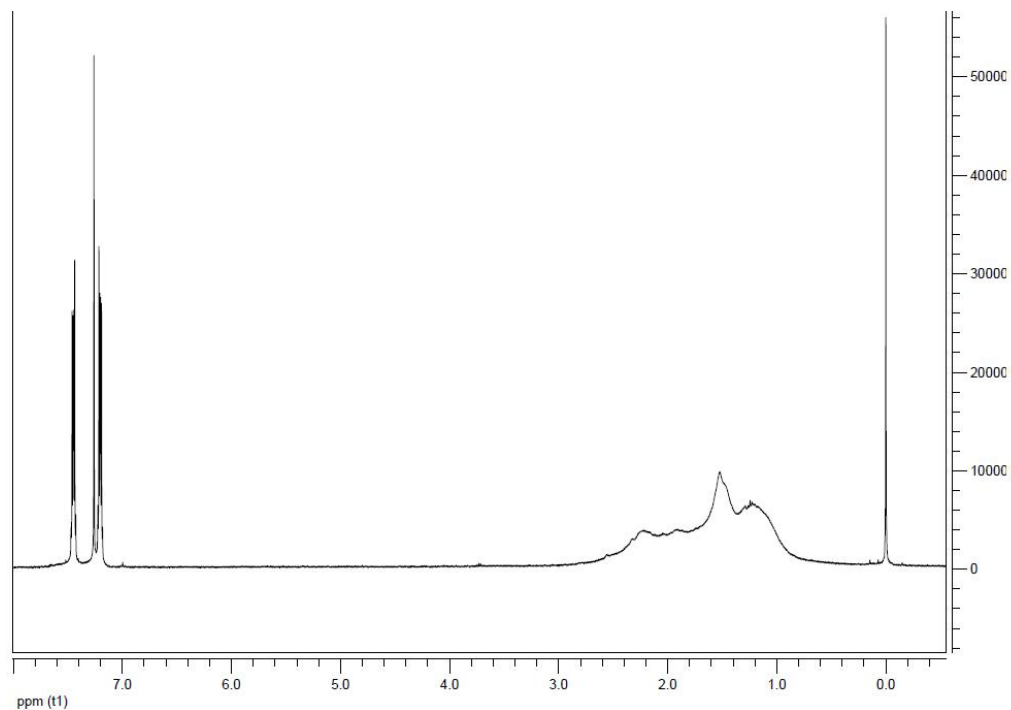


Figure S16. ¹H NMR (400 MHz, CDCl₃) spectra of norbornene homopolymers (Table 1 entry 8.).

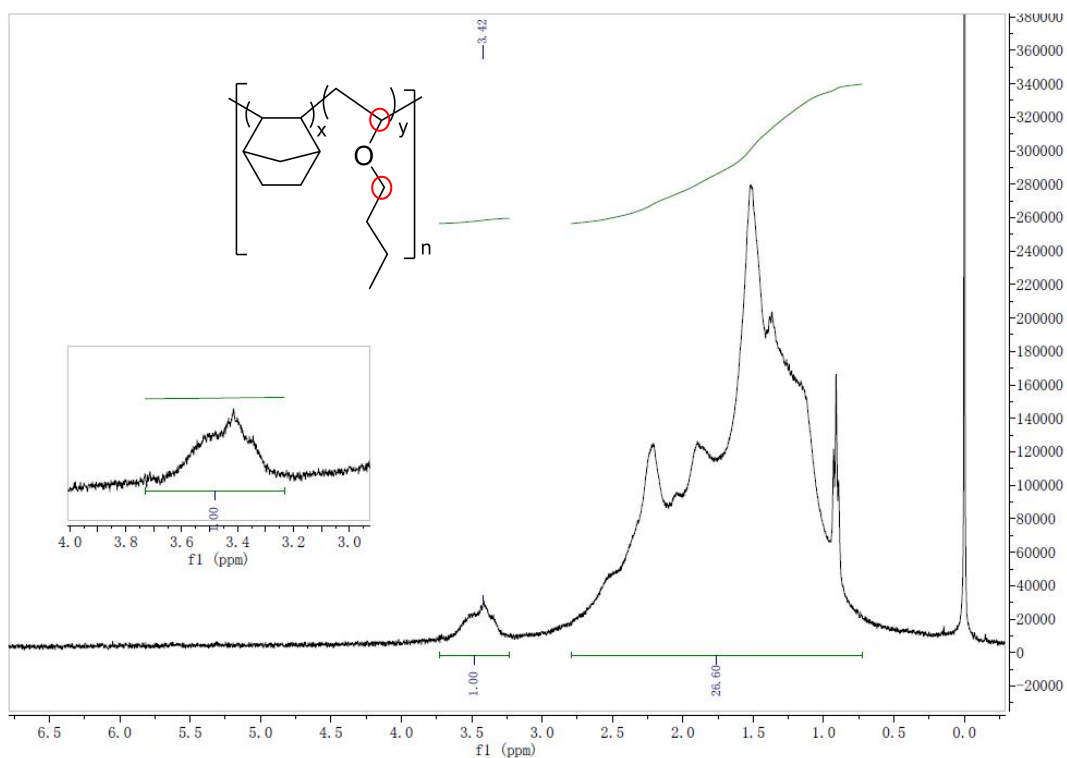


Figure S17. ¹H NMR (400 MHz, CDCl₃) spectra of NB-BVE copolymer obtained by **4c** (entry 2, Table 2).

The incorporation (mol%) of BVE in copolymer:

$$x = \frac{\frac{I_a}{3}}{\frac{I_a}{3} + \frac{I_b - \frac{I_a}{3} \times 9}{10}} \times 100\% = \frac{10I_a}{3I_b + I_a}$$

I_a – The integration of methylene (–CH₂–O–) and methyne (–CH–O–) in BVE units;

I_b – The integration of the peaks from 0.75–2.75 ppm.

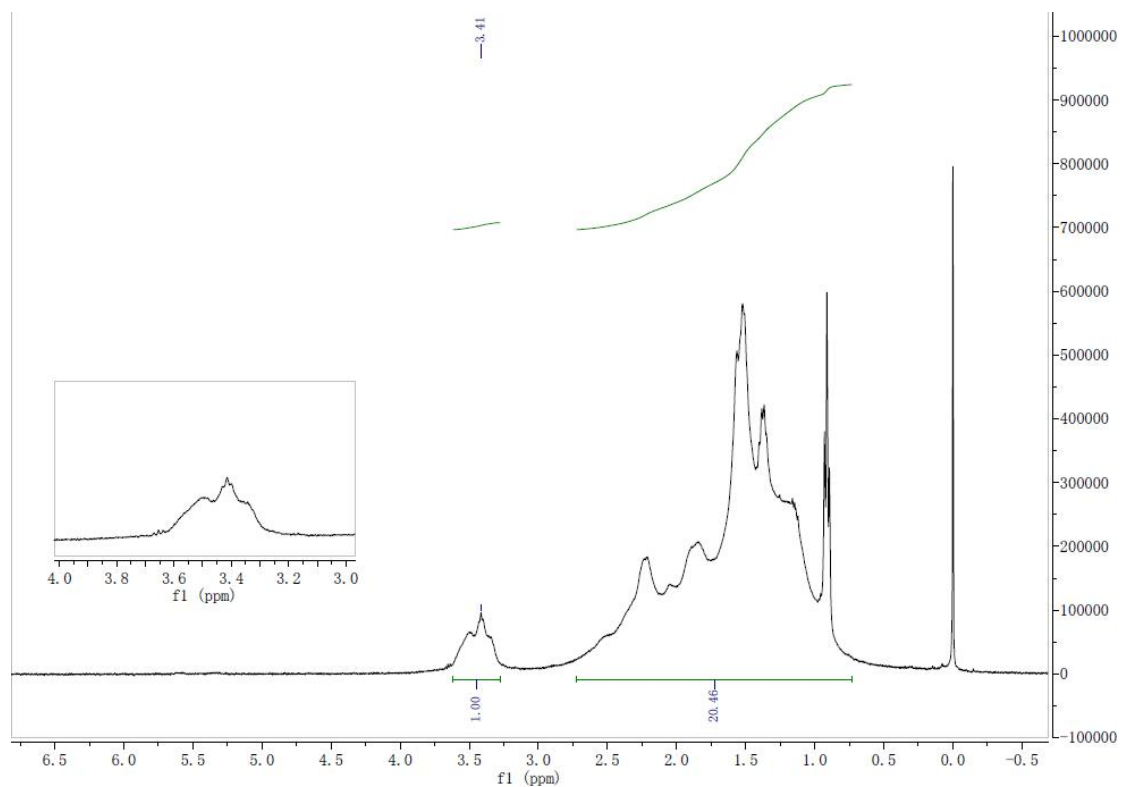


Figure S18. ^1H NMR (400 MHz, CDCl_3) spectra of NB-BVE copolymer obtained by **4c** (entry 3, Table 2).

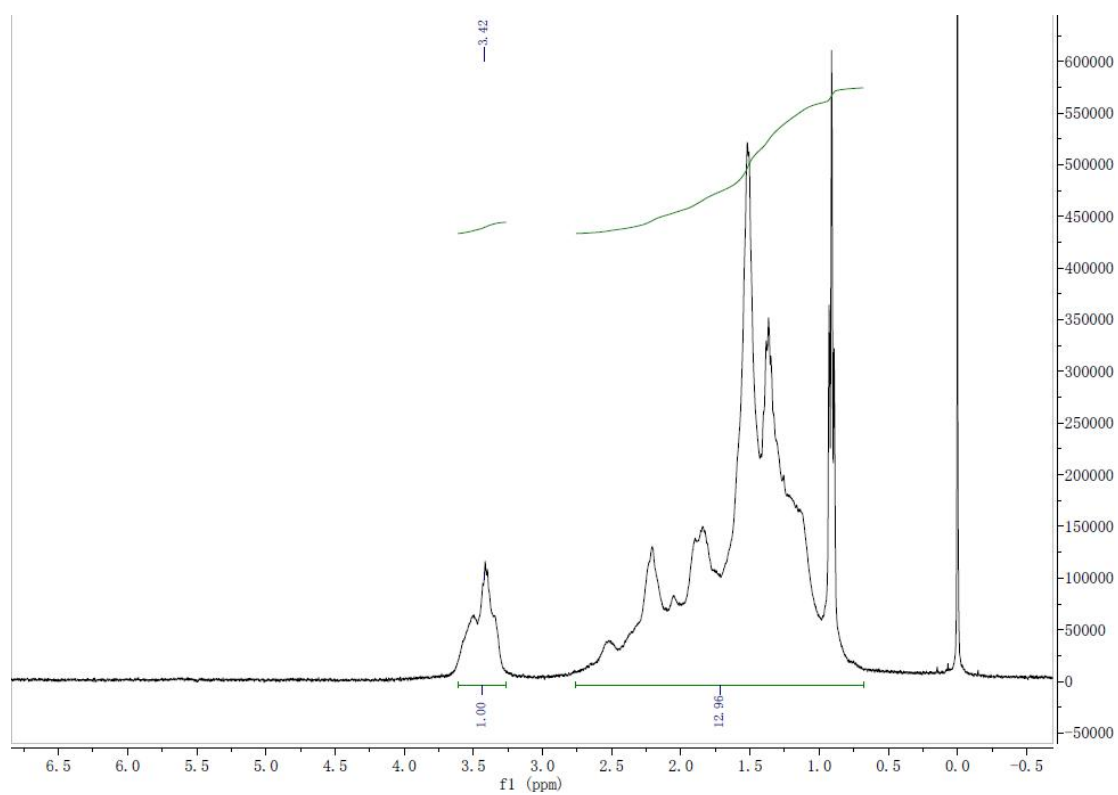


Figure S19. ^1H NMR (400 MHz, CDCl_3) spectra of NB-BVE copolymer obtained by **4c** (entry 4, Table 2).

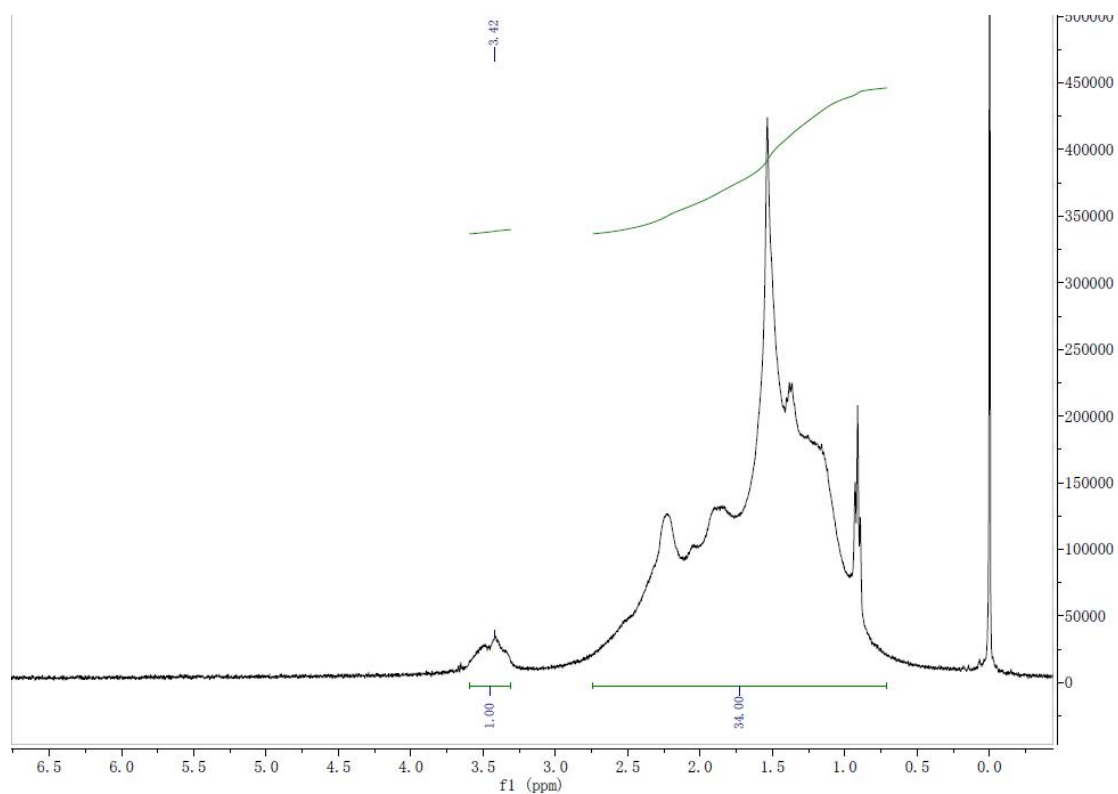


Figure S20. ¹H NMR (400 MHz, CDCl₃) spectra of NB-BVE copolymer obtained by **4a** (entry 6, Table 2).

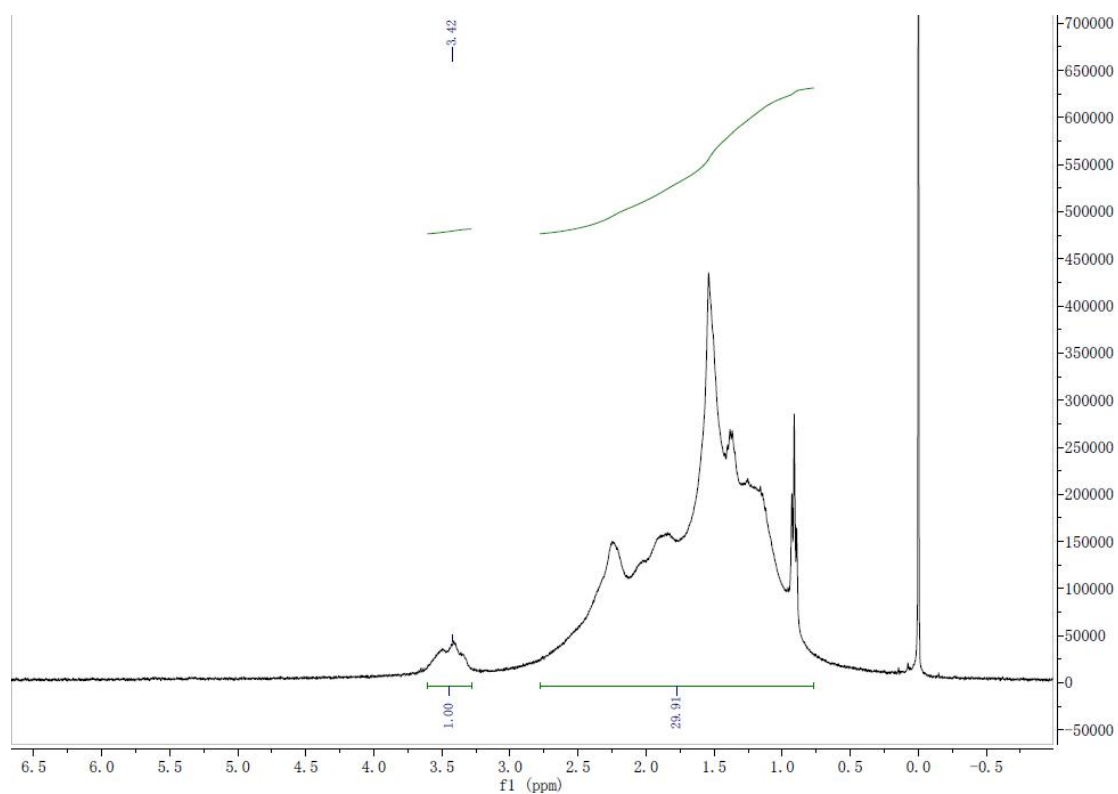


Figure S21. ¹H NMR (400 MHz, CDCl₃) spectra of NB-BVE copolymer obtained by **4b** (entry 7, Table 2).

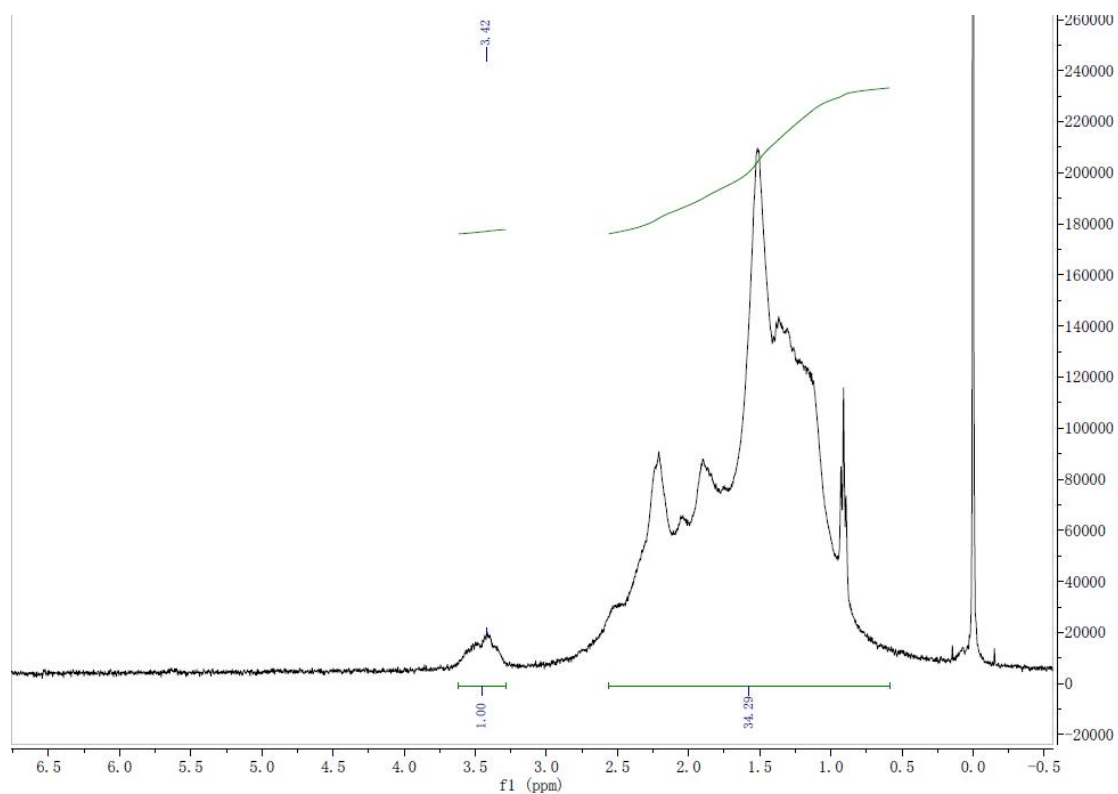


Figure S22. ^1H NMR (400 MHz, CDCl_3) spectra of NB-BVE copolymer obtained by **4d** (entry 8, Table 2).

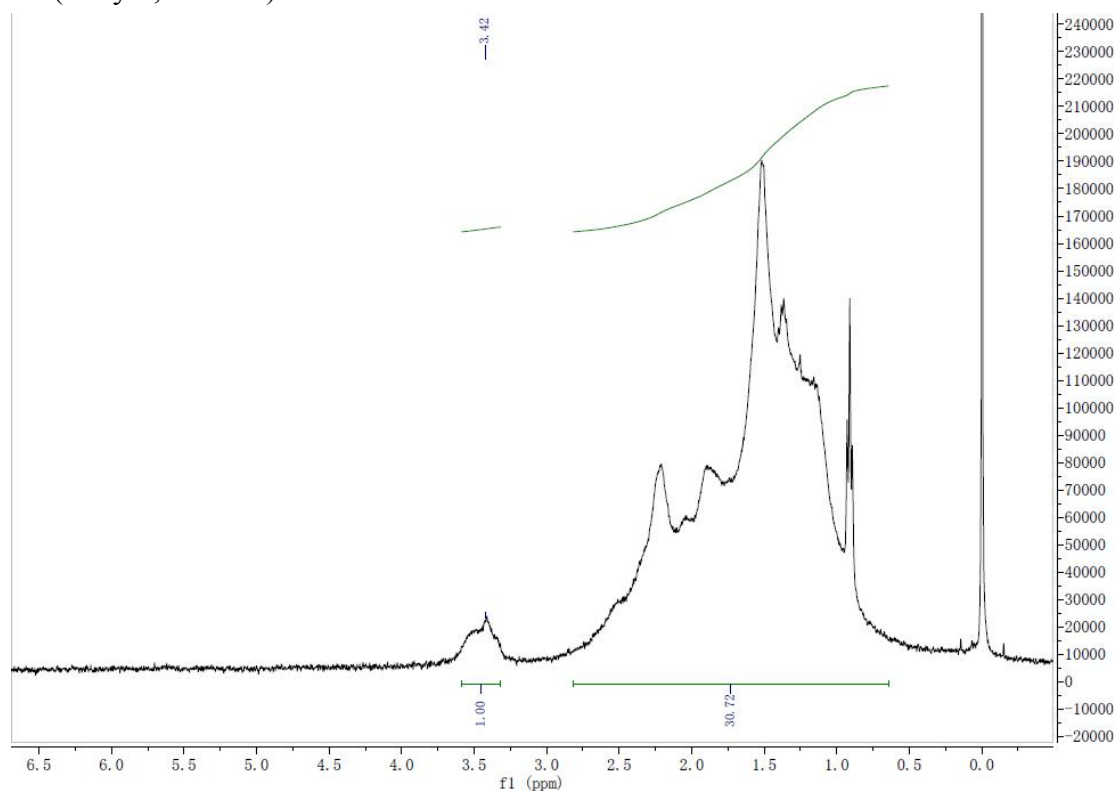


Figure S23. ^1H NMR (400 MHz, CDCl_3) spectra of NB-BVE copolymer obtained by **3** (entry 9, Table 2).

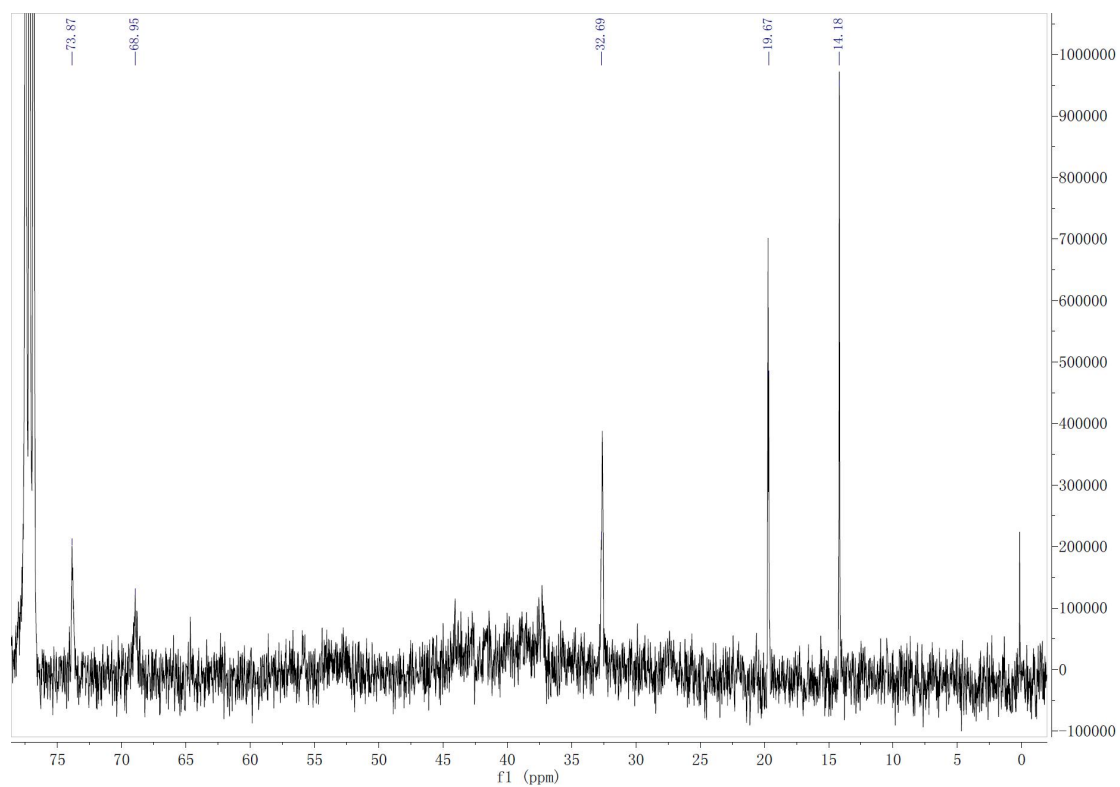


Figure S24. ^{13}C NMR (101 MHz, CDCl_3) spectra of NB-BVE copolymer obtained by **4c** (entry 4, Table 2).

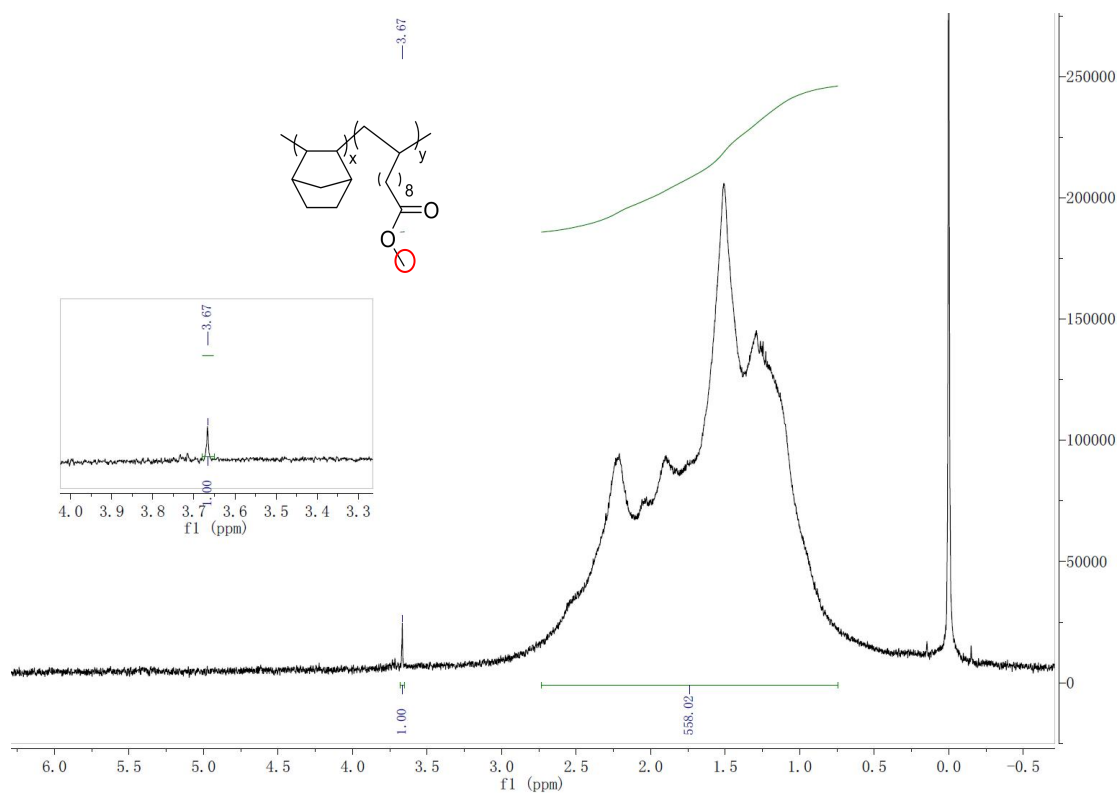


Figure S25. ¹H NMR (400 MHz, CDCl₃) spectra of NB-UA copolymer obtained by **4c** (entry 11, Table 2).

The incorporation (mol%) of UA in copolymer:

$$x = \frac{\frac{I_a}{3}}{\frac{I_a}{3} + \frac{I_b - \frac{I_a}{3} \times 19}{10}} \times 100\% = \frac{10I_a}{3I_b - 9I_a}$$

I_a – The integration of methyl (CH₃-O-) in UA units;

I_b – The integration of the peaks from 0.75–2.75 ppm.

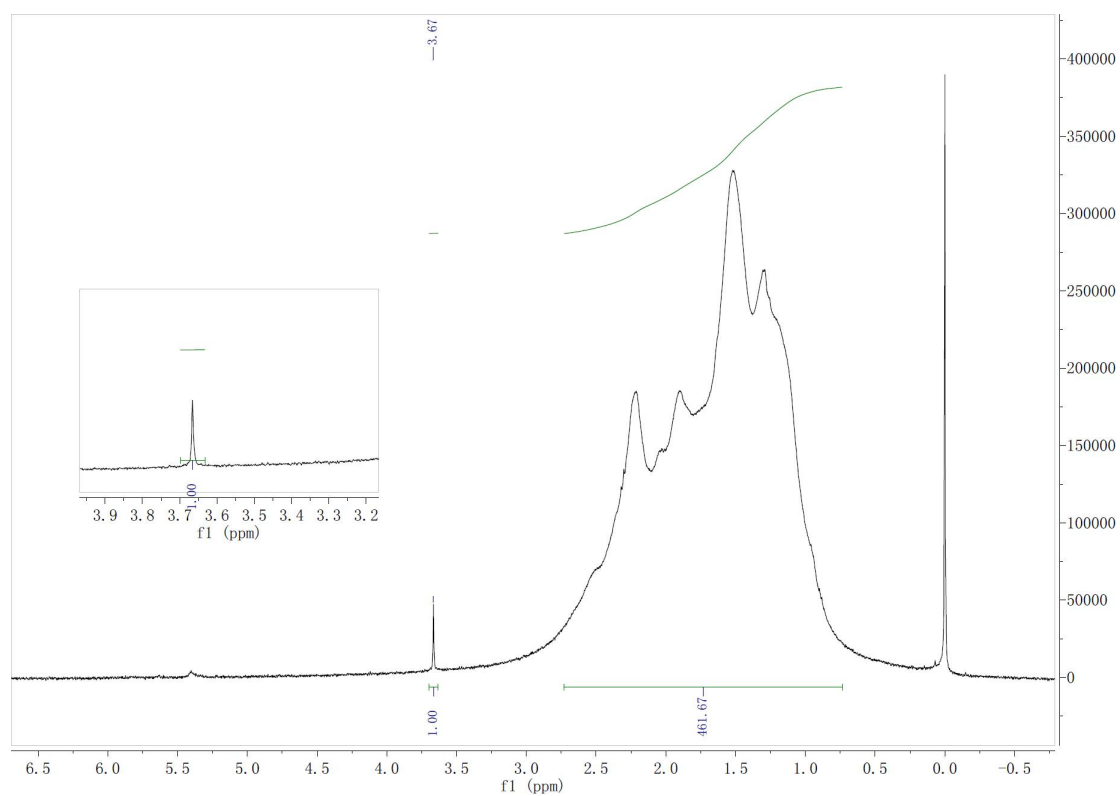


Figure S26. ^1H NMR (400 MHz, CDCl_3) spectra of NB-UA copolymer obtained by **4c** (entry 12, Table 2).

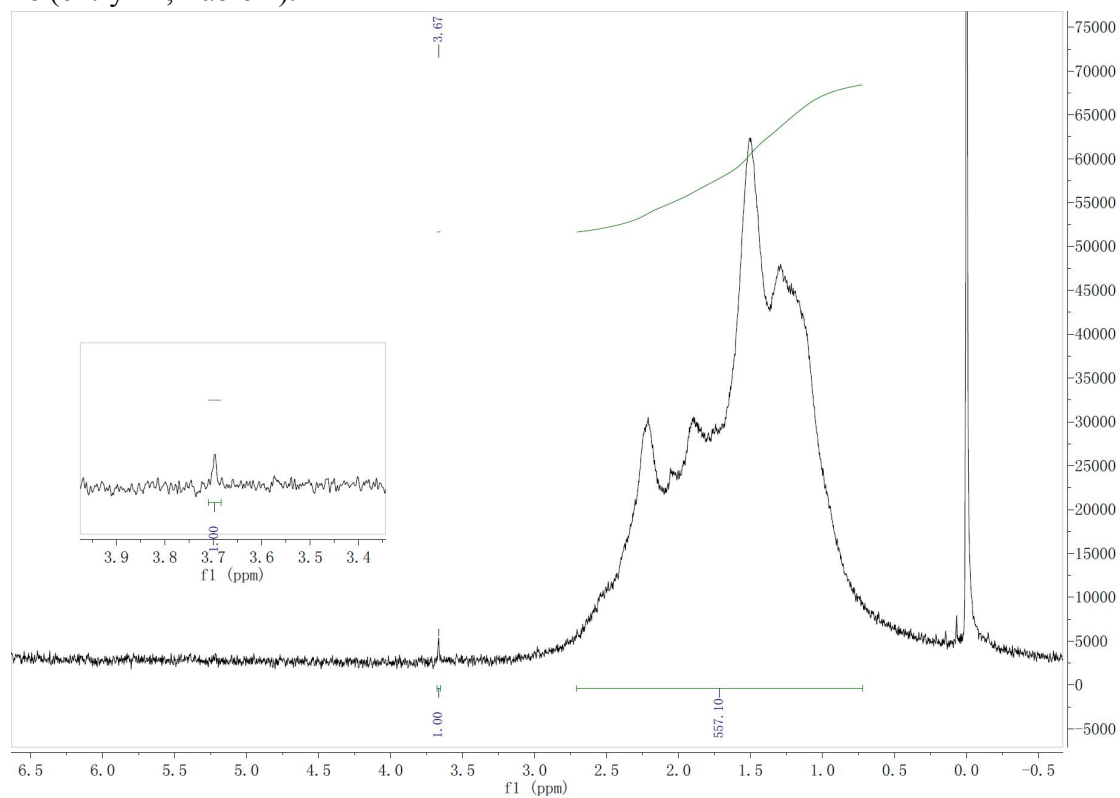


Figure S27. ^1H NMR (400 MHz, CDCl_3) spectra of NB-UA copolymer obtained by **4a** (entry 14, Table 2).

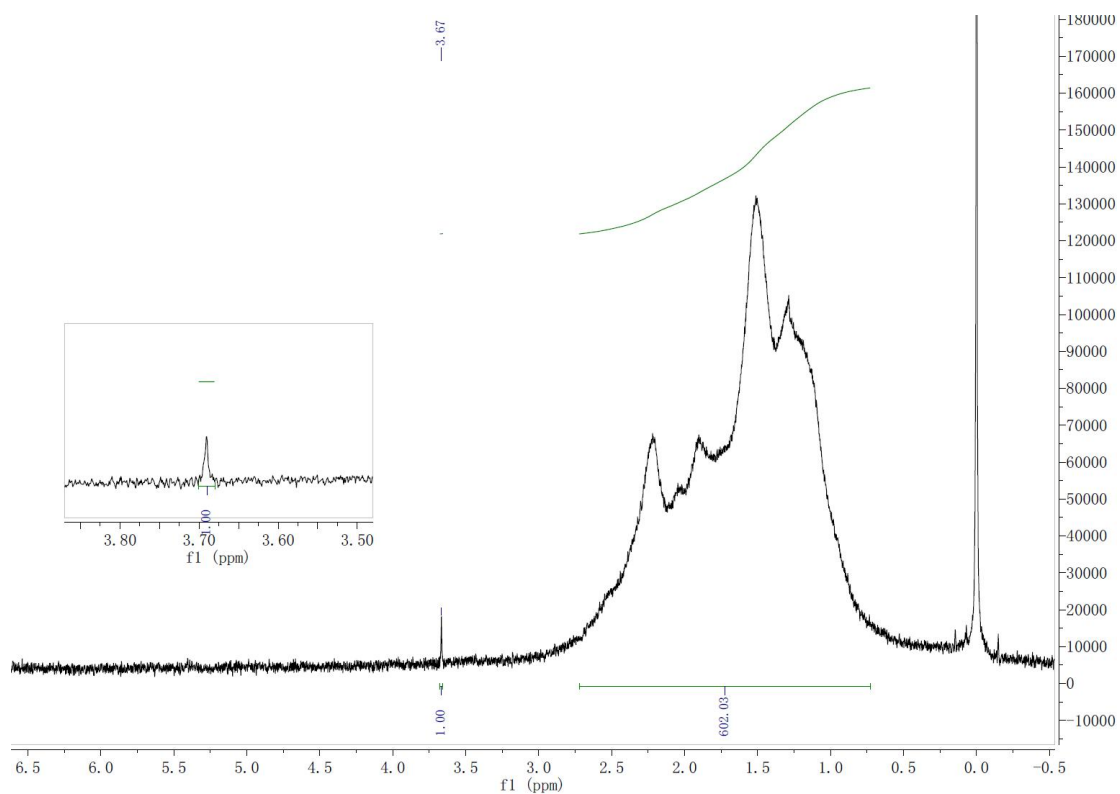


Figure S28. ^1H NMR (400 MHz, CDCl_3) spectra of NB-UA copolymer obtained by **4b** (entry 15, Table 2).

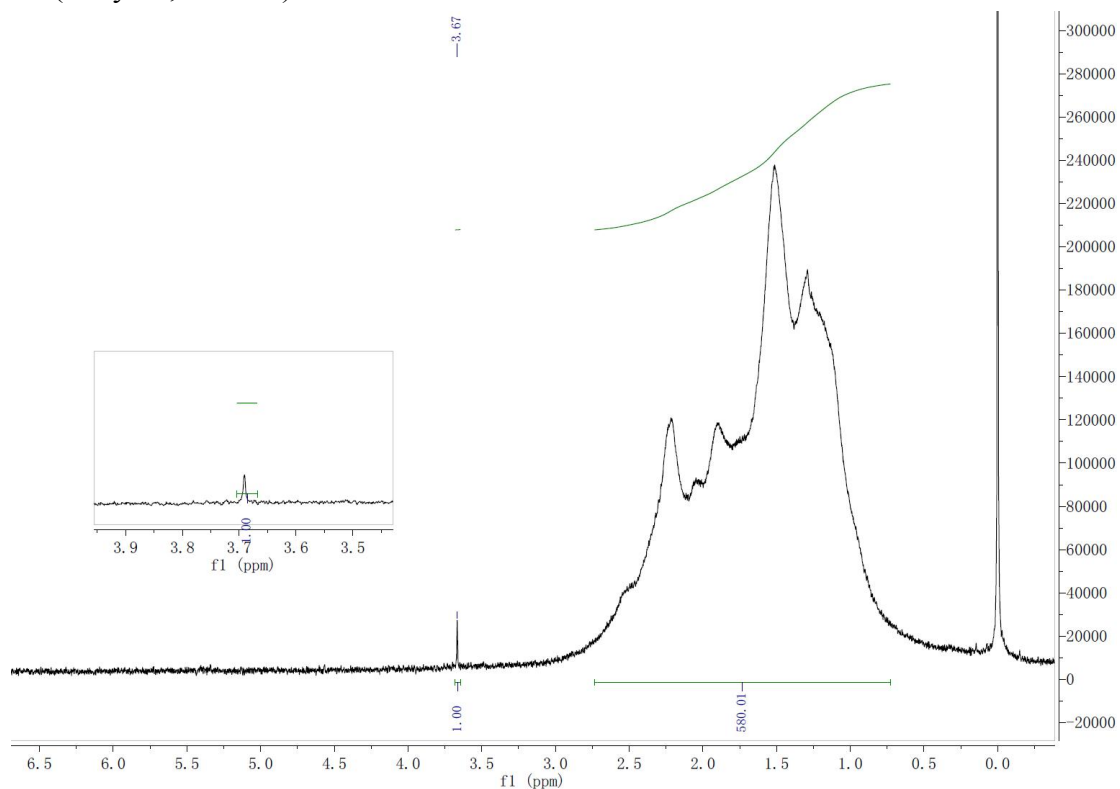


Figure S29. ^1H NMR (400 MHz, CDCl_3) spectra of NB-UA copolymer obtained by **4d** (entry 16, Table 2).

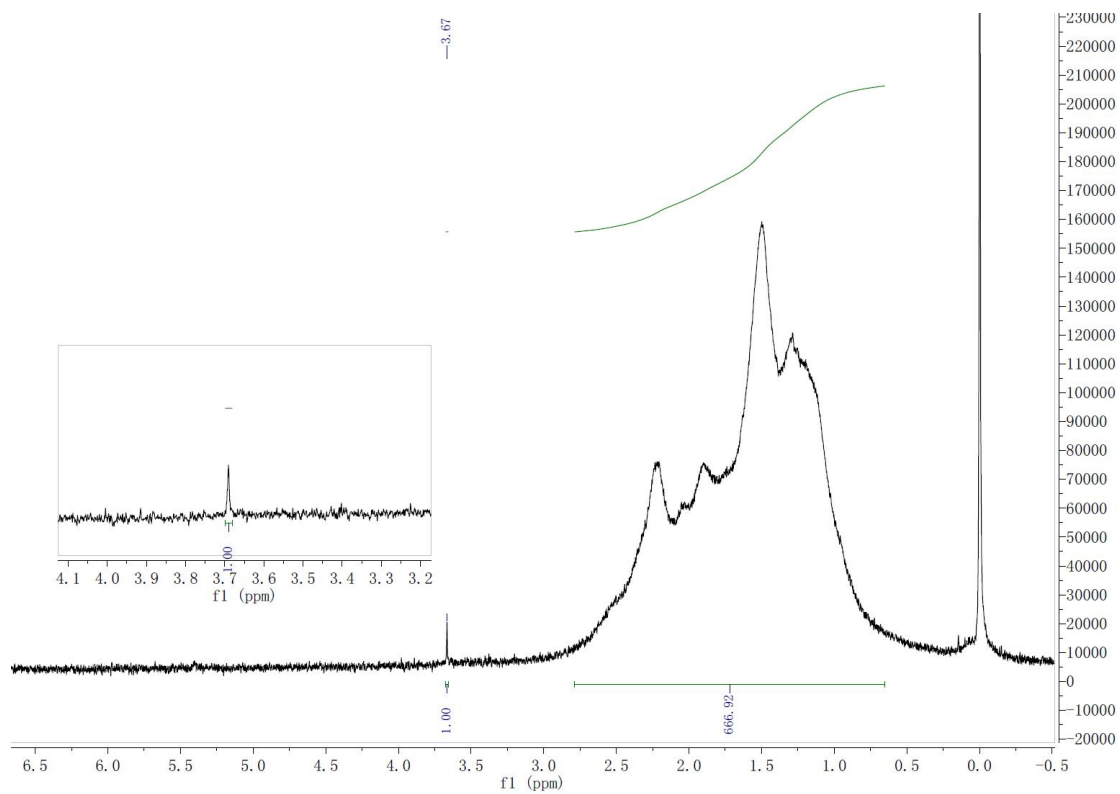
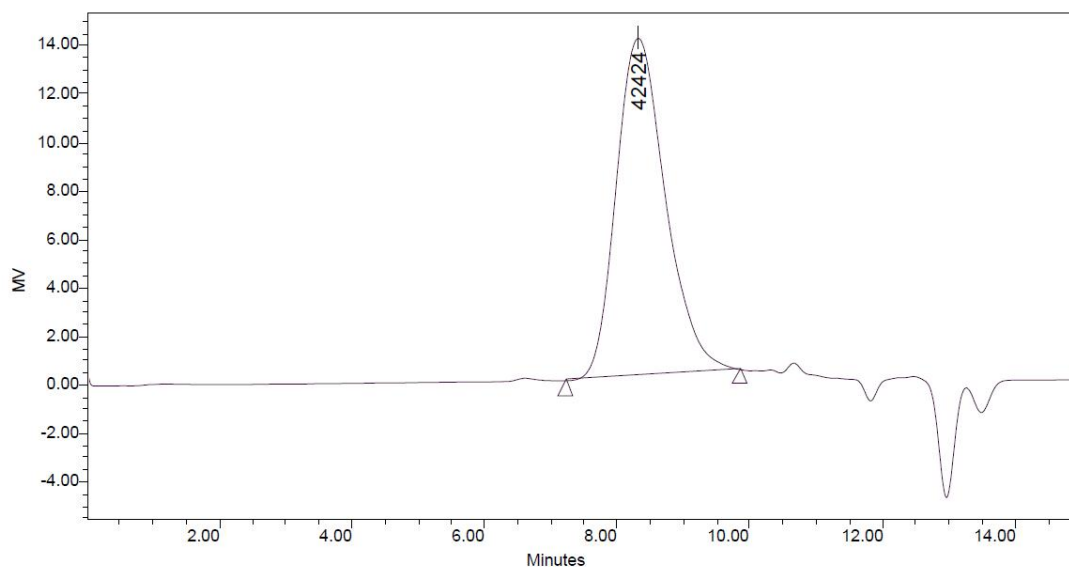


Figure S30. ^1H NMR (400 MHz, CDCl_3) spectra of NB-UA copolymer obtained by **3** (entry 17, Table 2).

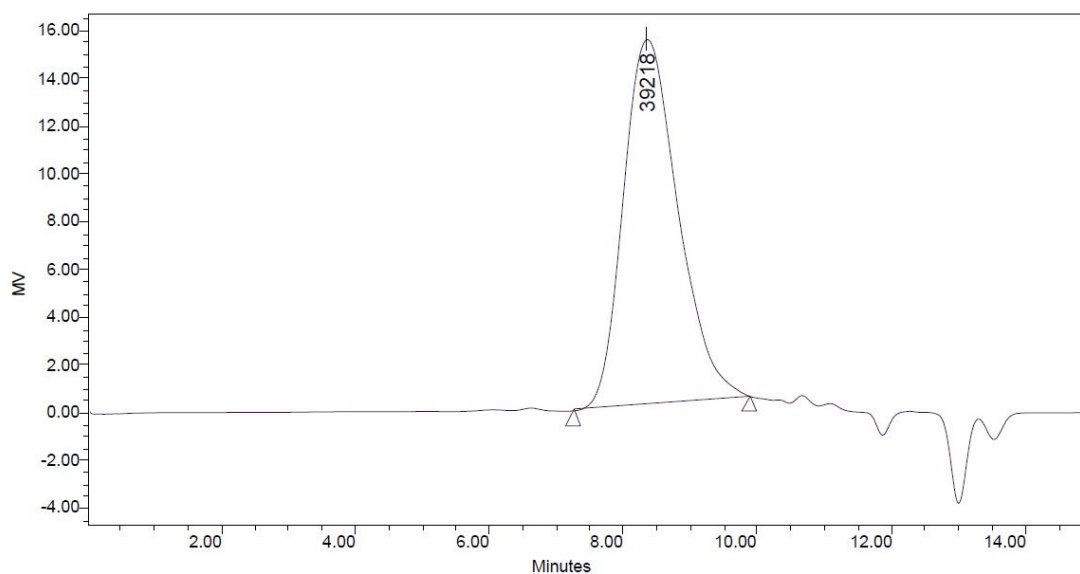
4. GPC curves of polymers



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	27737	45039	42424	64903	86662	1.623798	1.441061	1.924164

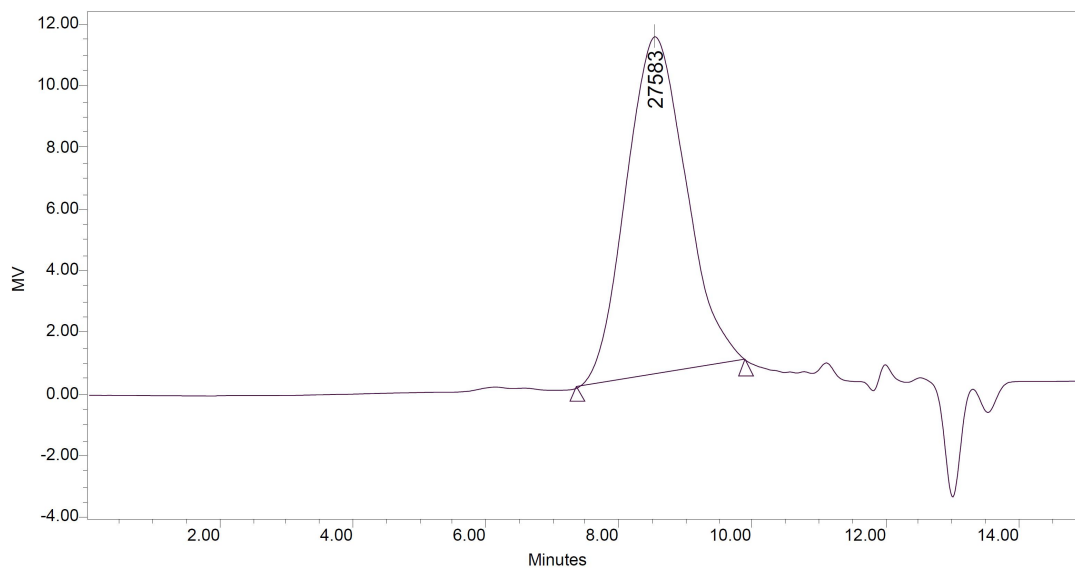
Figure S31. GPC curve of NB-BVE copolymer obtained by table 2 entry 2.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	24143	42100	39218	64084	88868	1.743802	1.522180	2.110881

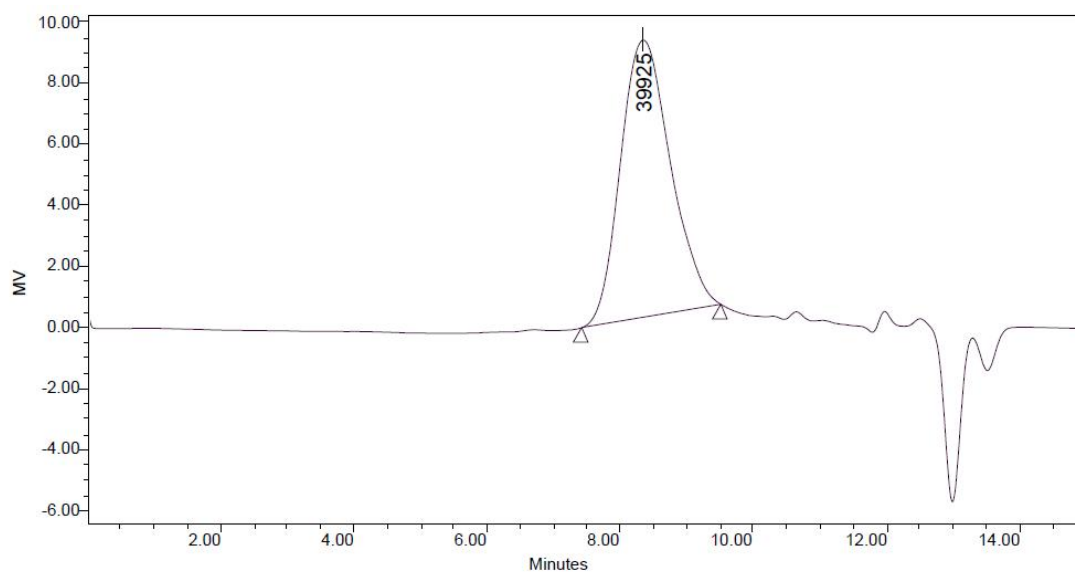
Figure S32. GPC curve of NB-BVE copolymer obtained by table 2 entry 3.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	18480	34683	27583	58814	87801	1.876769	1.695722	2.531505

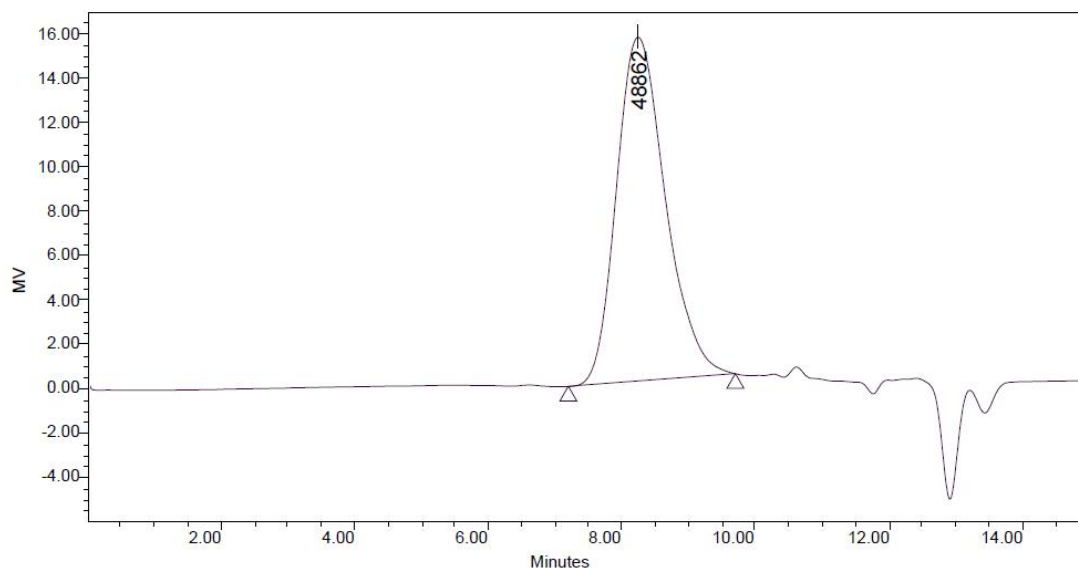
Figure S33. GPC curve of NB-BVE copolymer obtained by table 2 entry 4.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	28161	43397	39925	61937	81964	1.540995	1.427236	1.888713

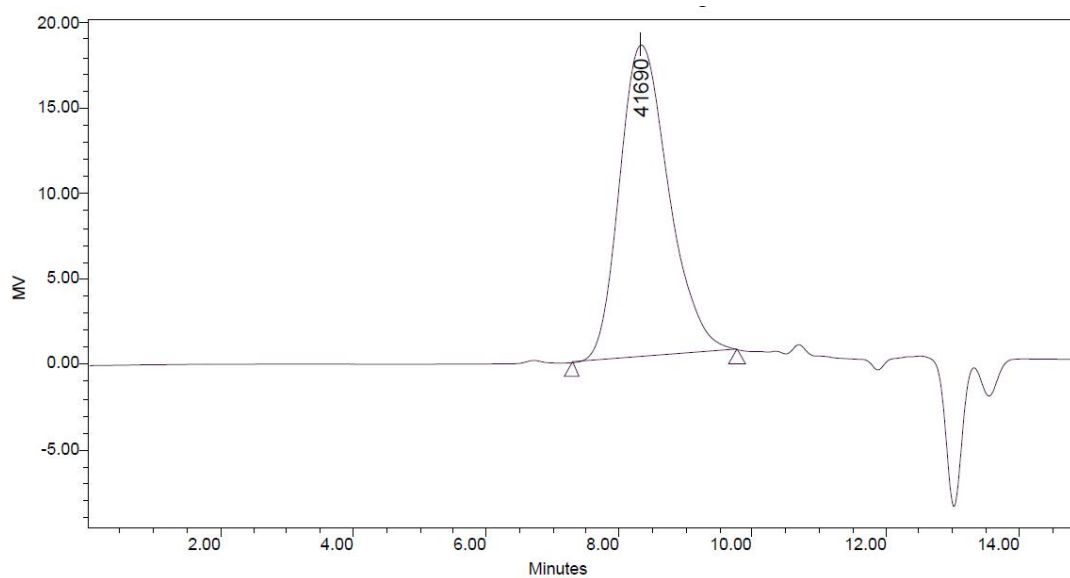
Figure S34. GPC curve of NB-BVE copolymer obtained by table 2 entry 6.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	32211	51225	48862	73205	97275	1.590291	1.429099	1.898985

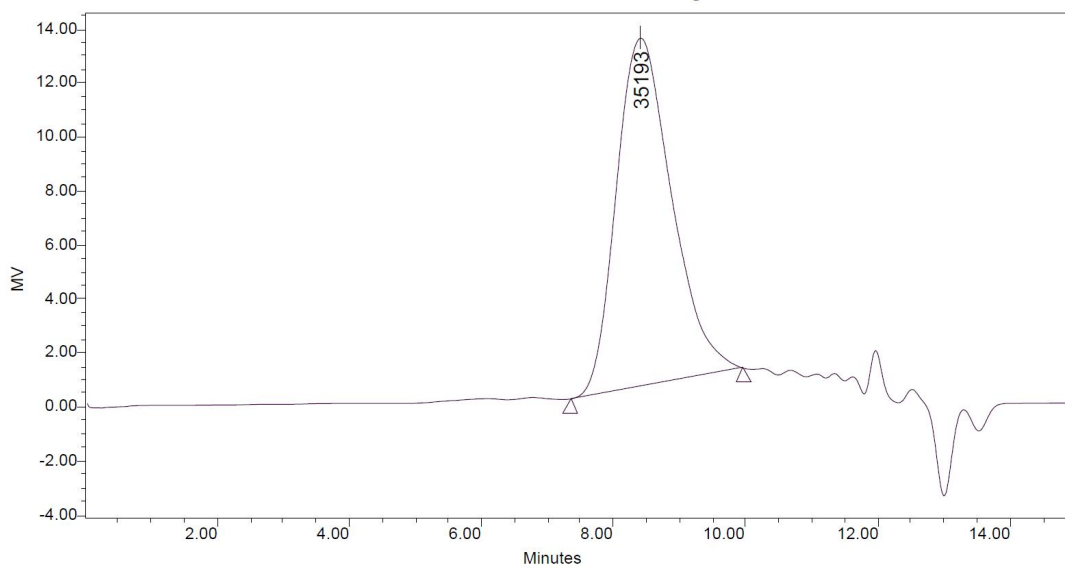
Figure S35. GPC curve of NB-BVE copolymer obtained by table 2 entry 7.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	27516	43779	41690	62774	83771	1.591023	1.433900	1.913497

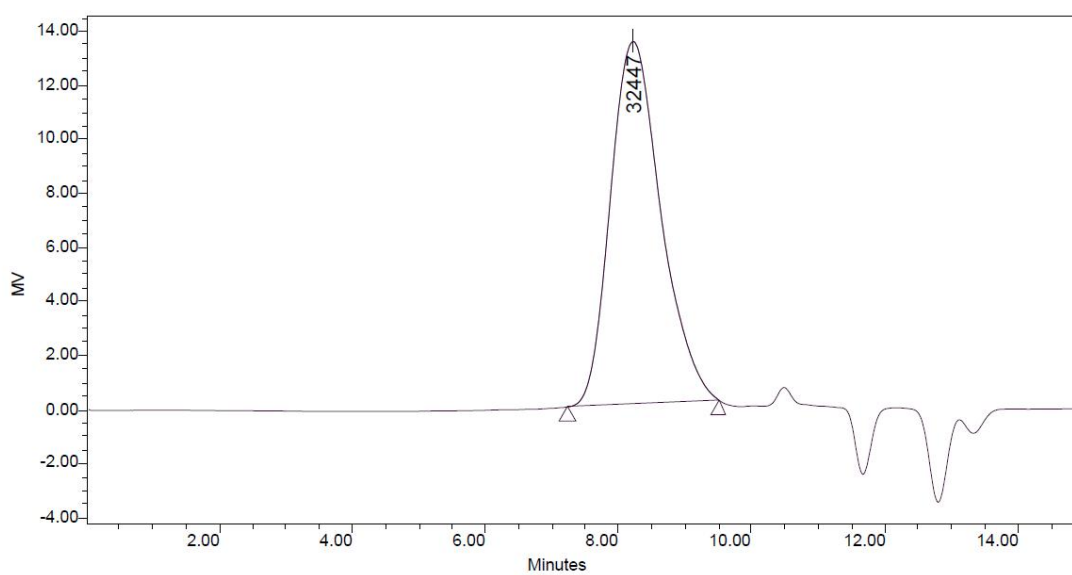
Figure S36. GPC curve of NB-BVE copolymer obtained by table 2 entry 8.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	21148	37927	35193	58048	79585	1.793362	1.530538	2.098381

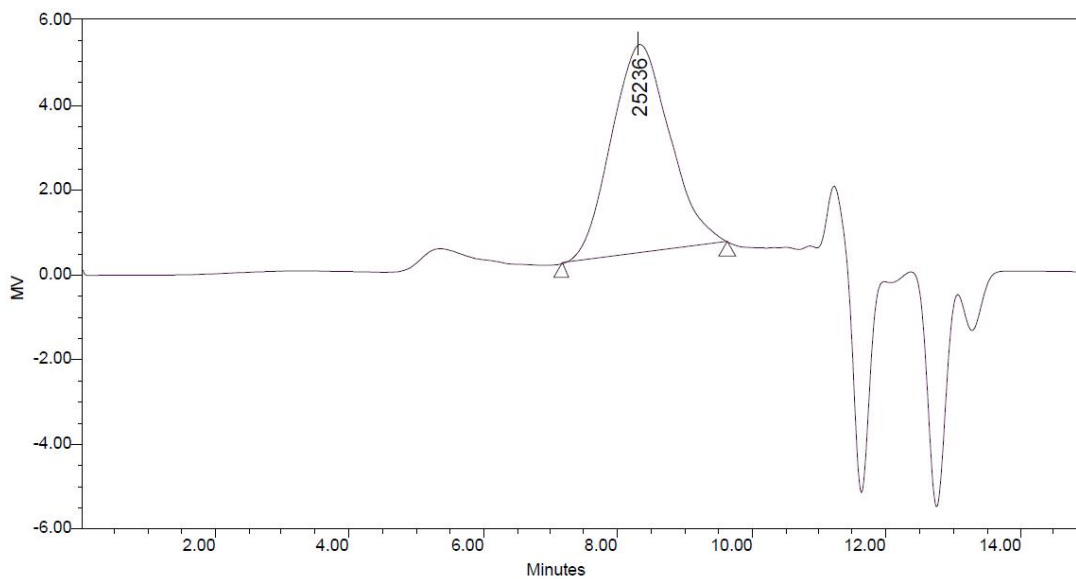
Figure S37. GPC curve of NB-BVE copolymer obtained by table 2 entry 9.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	19599	35885	32447	56152	78016	1.830949	1.564787	2.174086

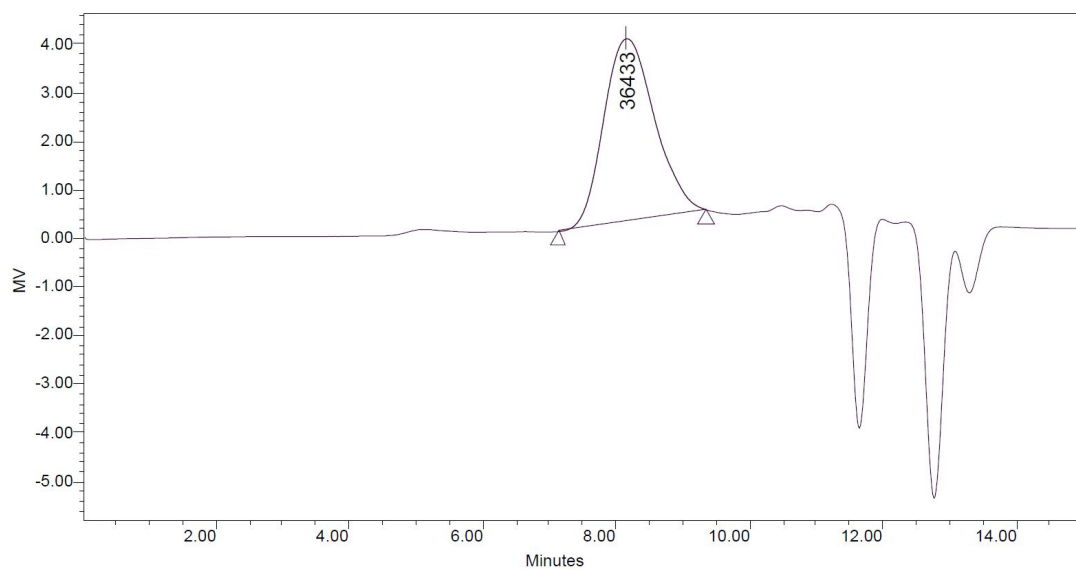
Figure S38. GPC curve of NB-UA copolymer obtained by Table 2 entry 11.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	15732	33861	25236	62263	95707	2.152355	1.836778	2.826438

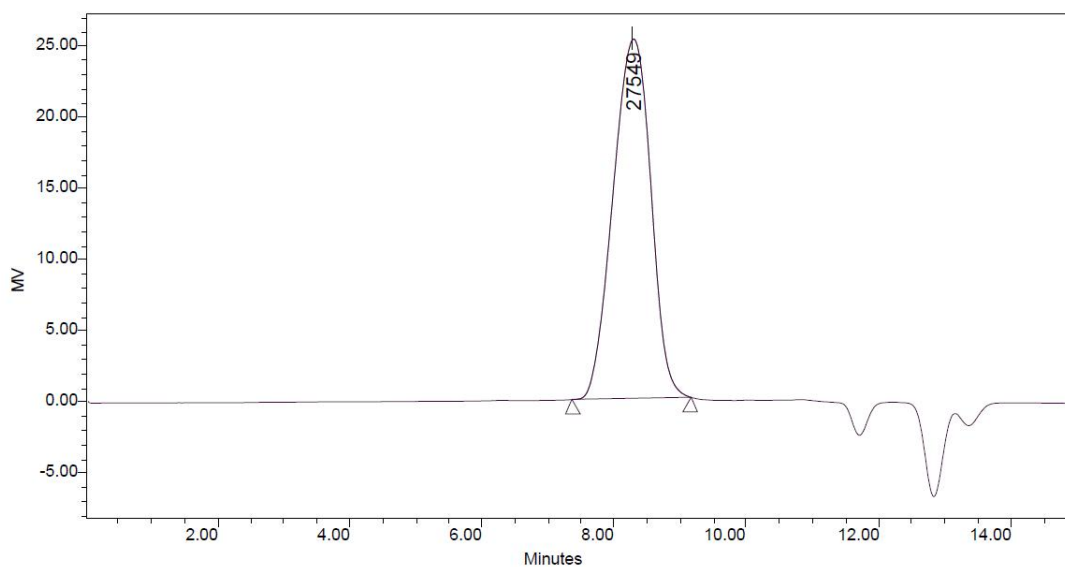
Figure S39. GPC curve of NB-UA copolymer obtained by Table 2 entry 12.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	23328	41180	36433	63925	88518	1.765279	1.552324	2.149525

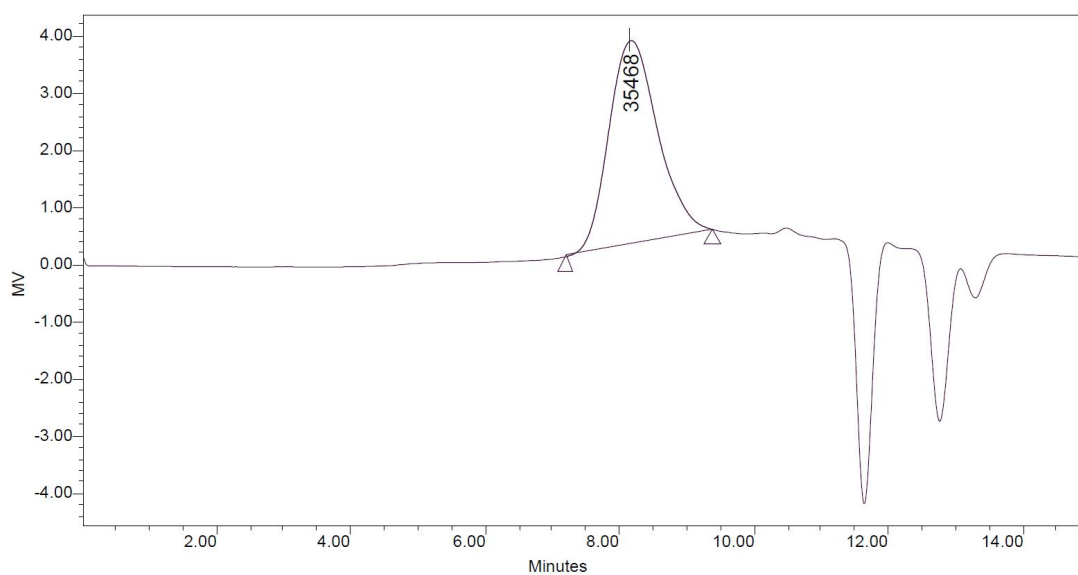
Figure S40. GPC curve of NB-UA copolymer obtained by Table 2 entry 14.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		25185	34187	27549	45854	59224	1.357417	1.341280	1.732357

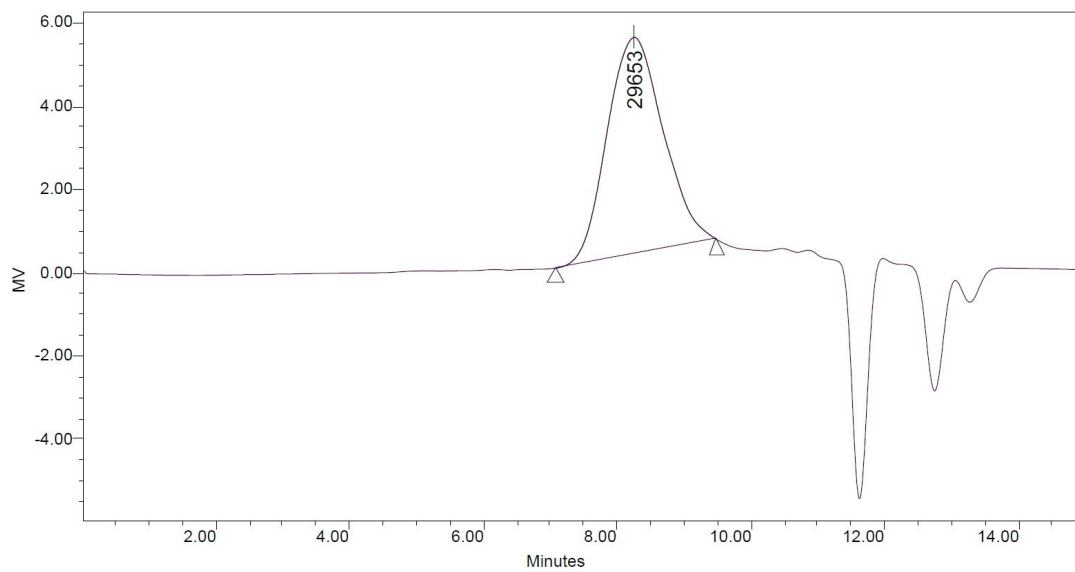
Figure S41. GPC curve of NB-UA copolymer obtained by Table 2 entry 15.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		23145	40007	35468	61048	84242	1.728531	1.525931	2.105667

Figure S42. GPC curve of NB-UA copolymer obtained by Table 2 entry 16.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		18989	37703	29653	64800	96374	1.985485	1.718694	2.556118

Figure S43. GPC curve of NB-UA copolymer obtained by Table 2 entry 17.

5. TGA curves of polymers.

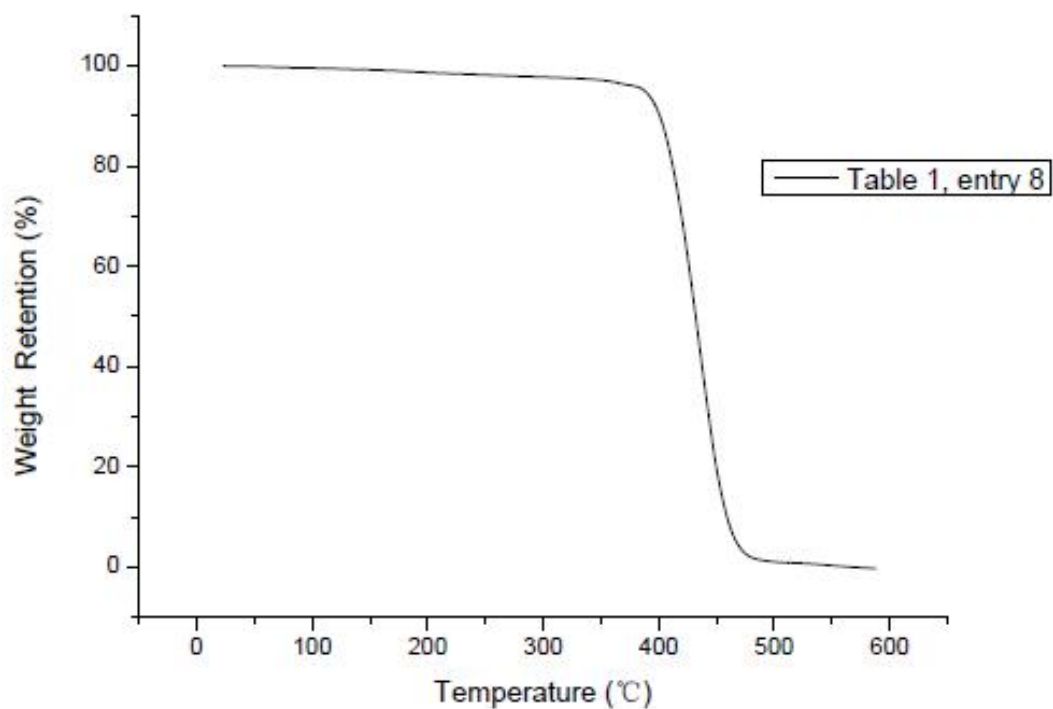


Figure S44. TGA of PNBs.

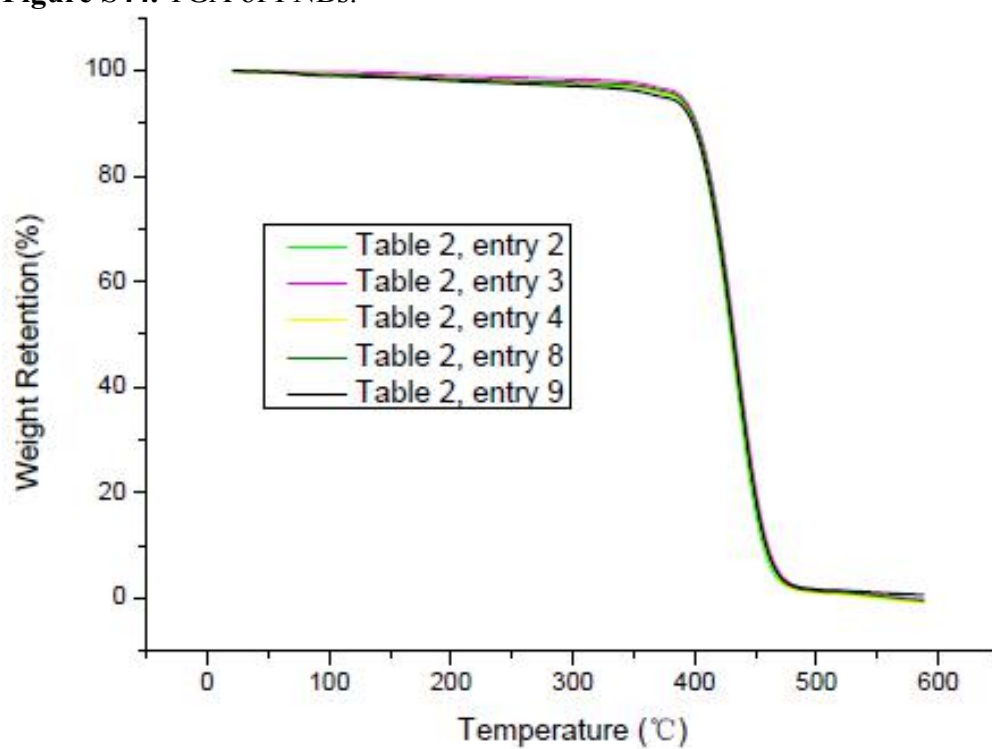


Figure S45. TGA of NB-BVE copolymer.

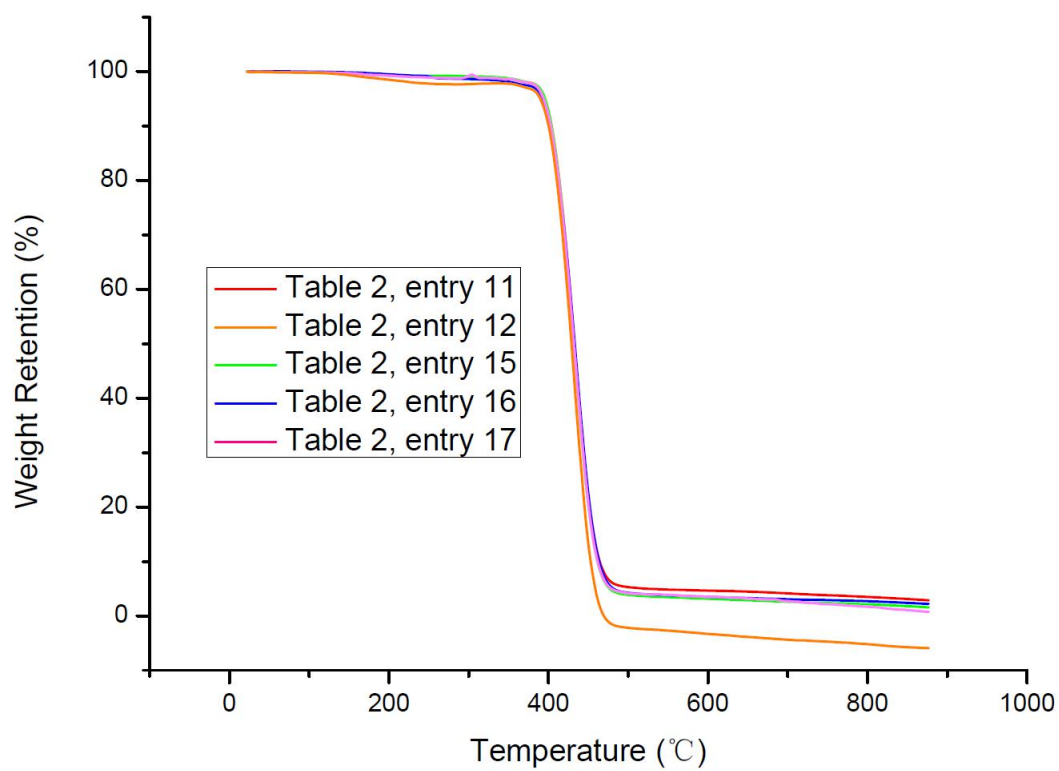


Figure S46. TGA of NB-UA copolymer.

6. DSC curves of polymers

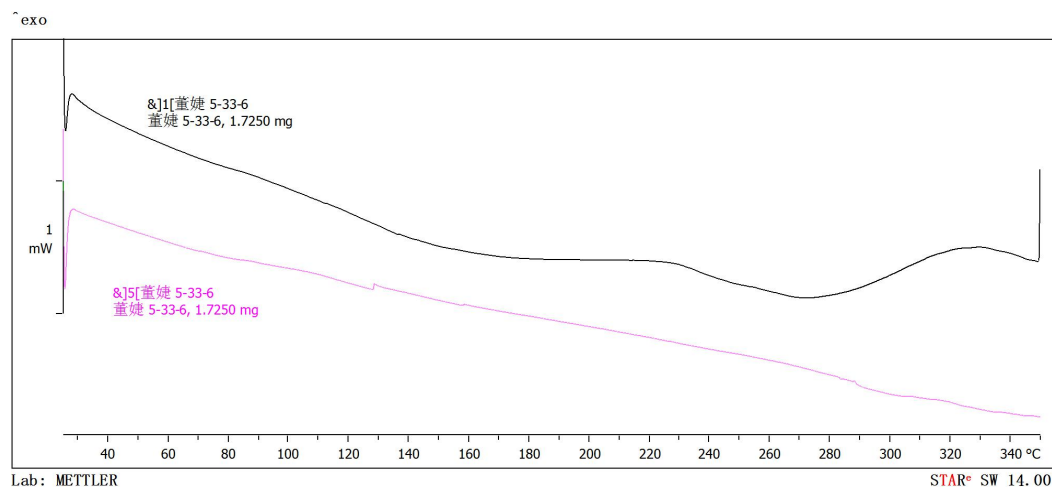


Figure S47. DSC thermograms of PNB obtained by Table 1 entry 8.

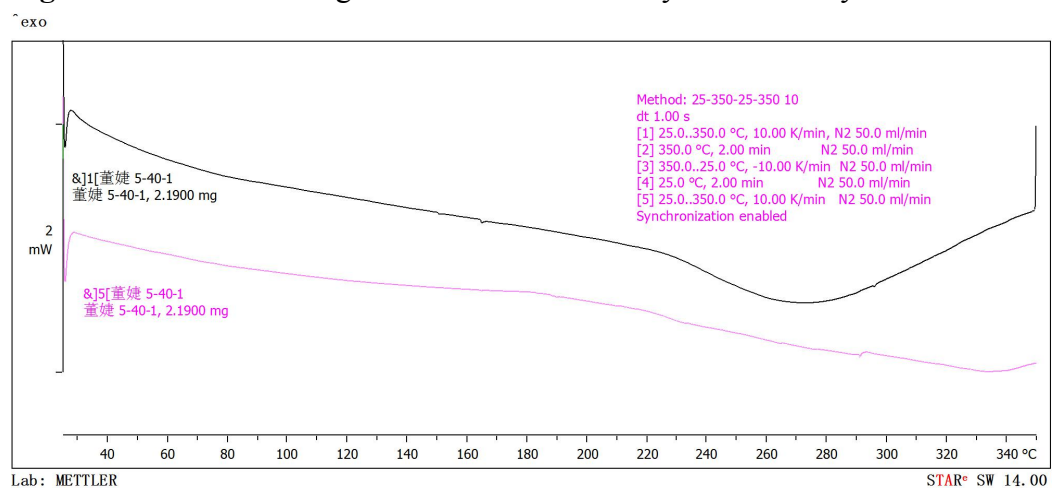


Figure S48. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 2.

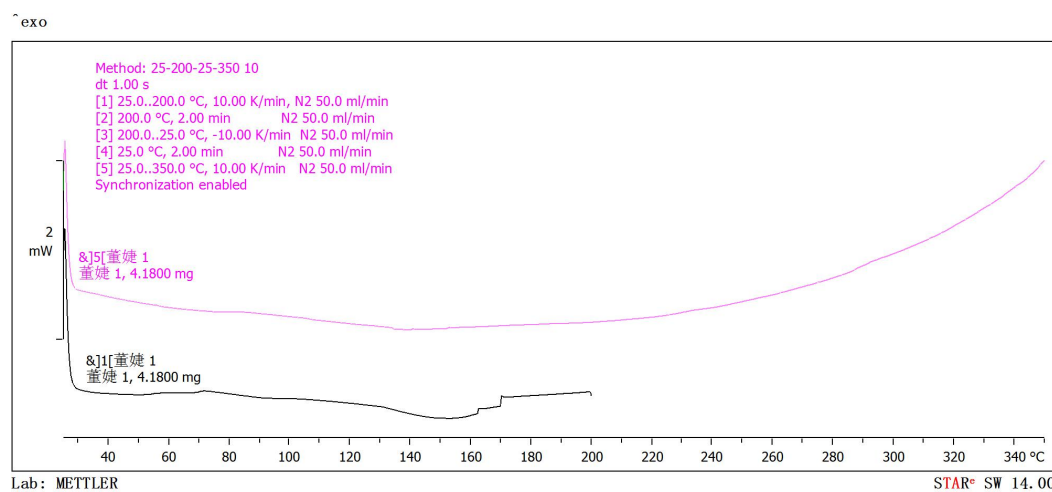


Figure S49. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 3.

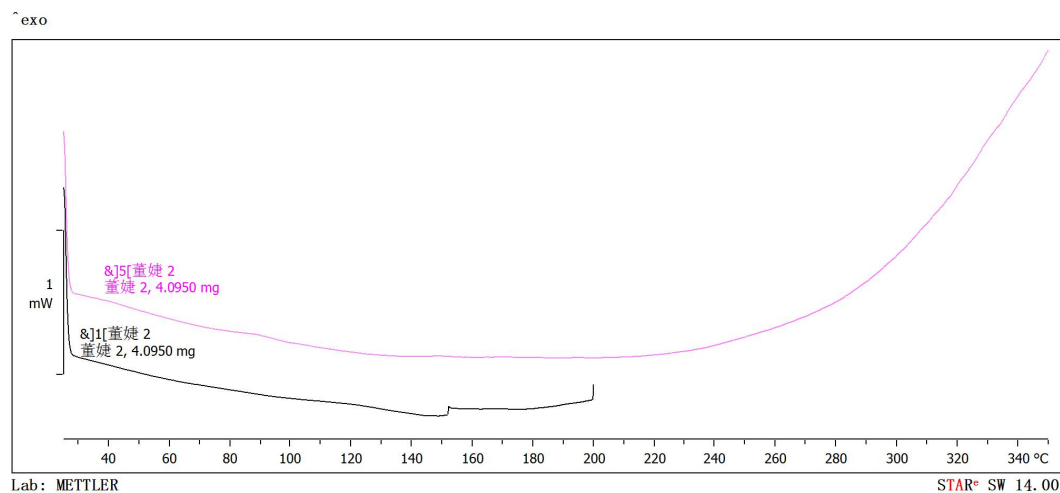


Figure S50. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 4.

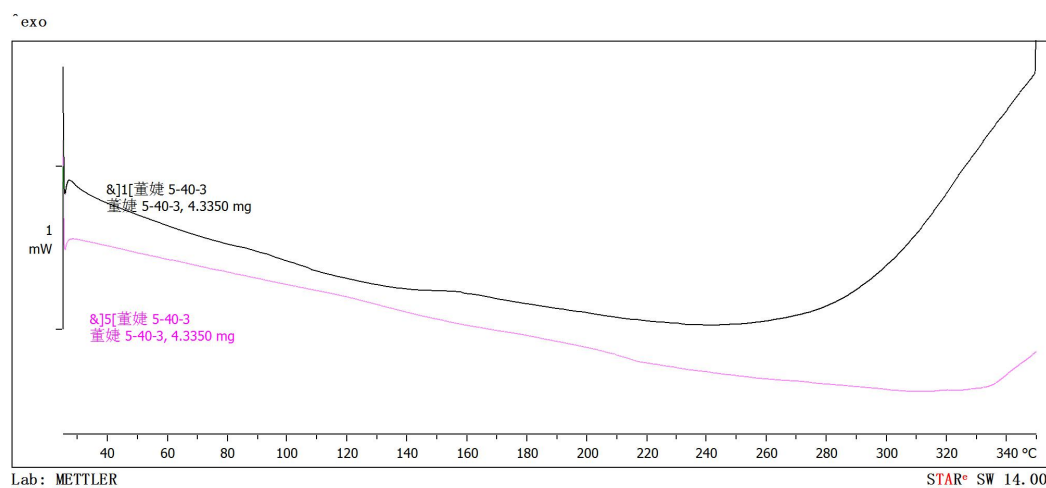


Figure S51. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 6.

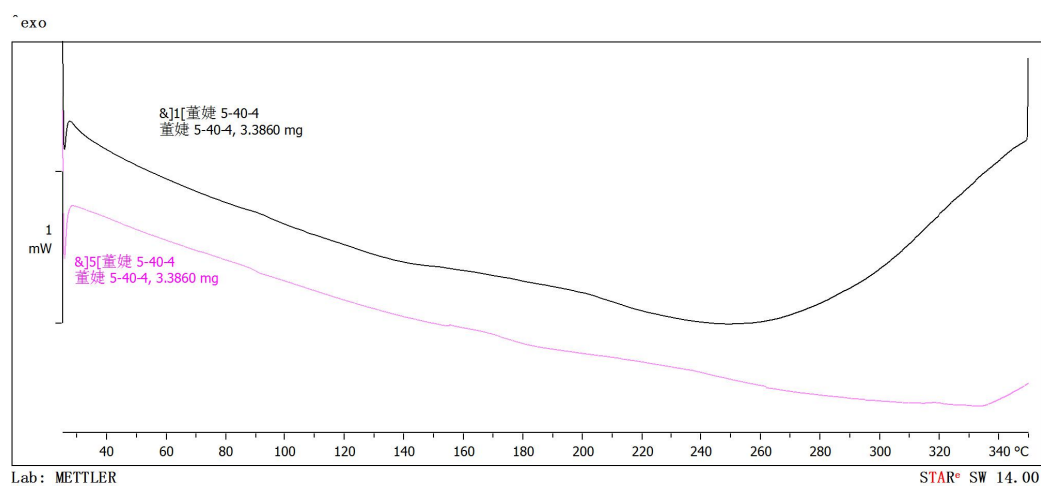


Figure S52. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 7.

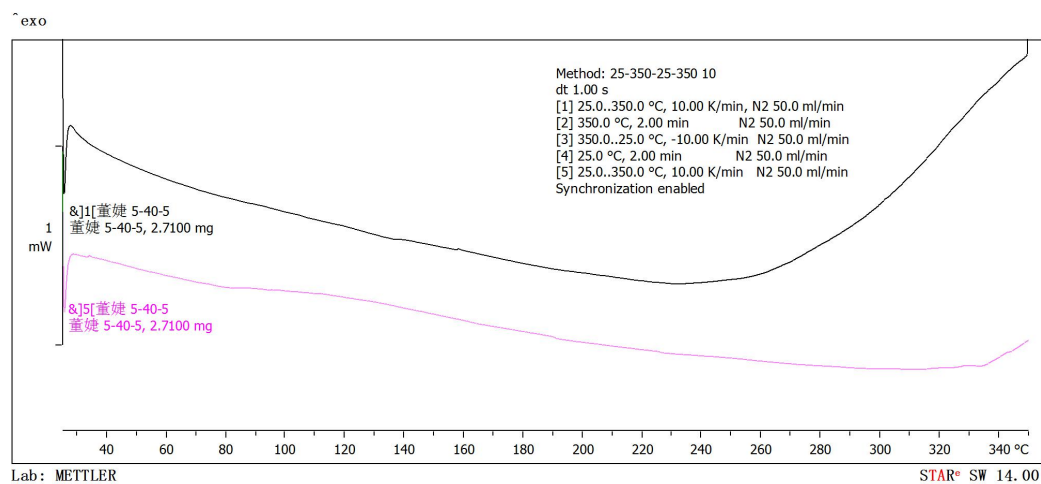


Figure S53. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 8.

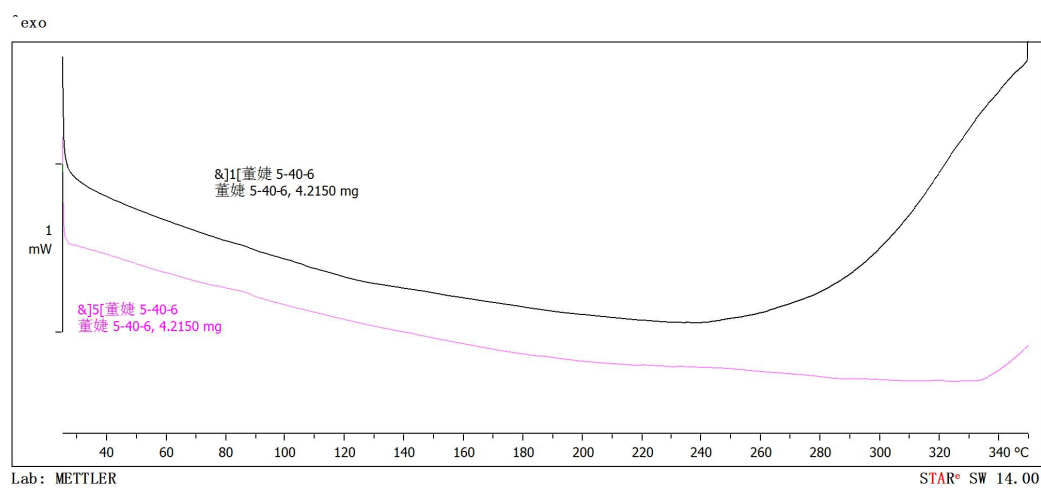


Figure S54. DSC thermograms of NB-BVE copolymer obtained by table 2 entry 9.

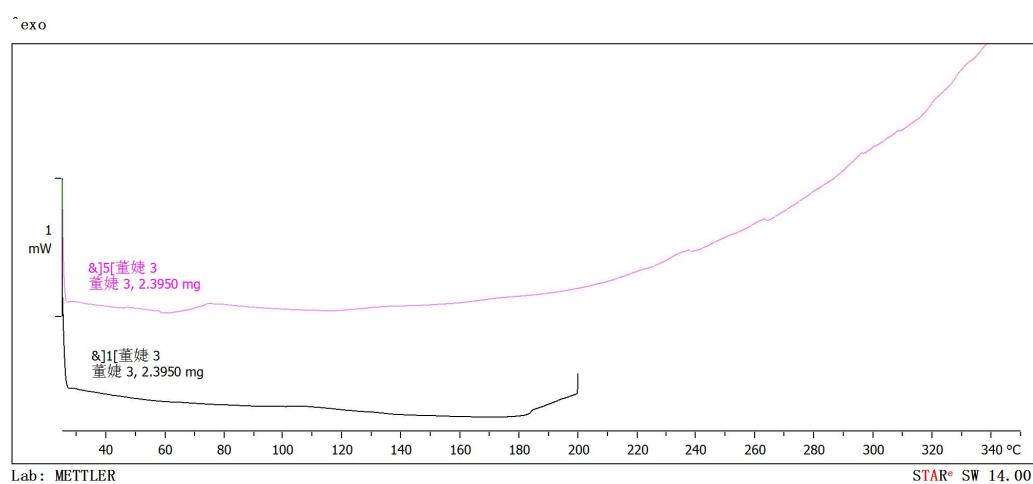


Figure S55. DSC thermograms of NB-UA copolymer obtained by Table 2 entry 11.

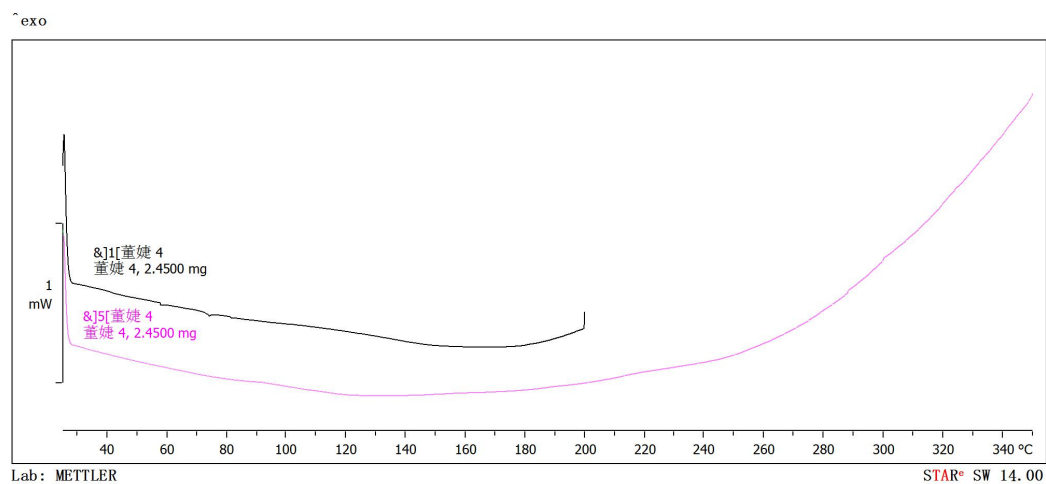


Figure S56. DSC thermograms of NB-UA copolymer obtained by Table 2 entry 12.

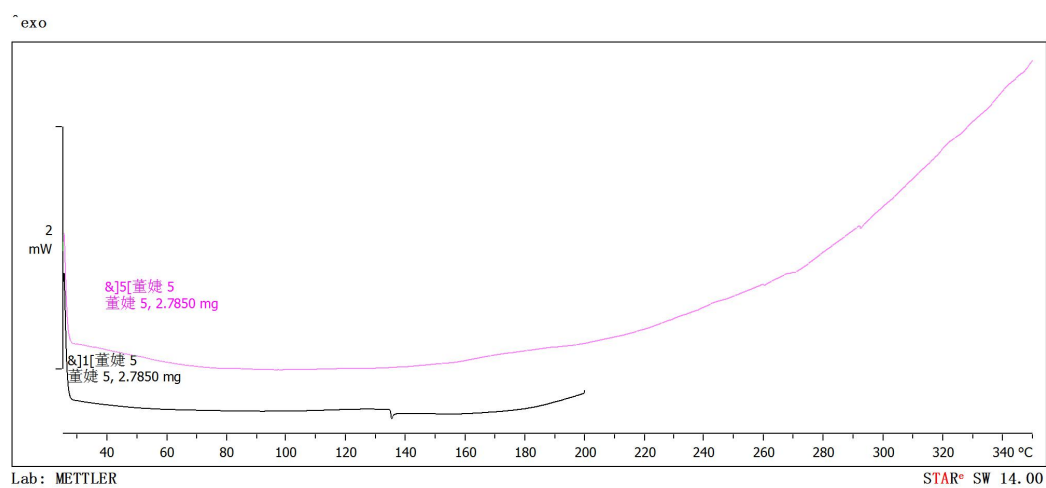


Figure S57. DSC thermograms of NB-BVE copolymer obtained by Table 2 entry 14.

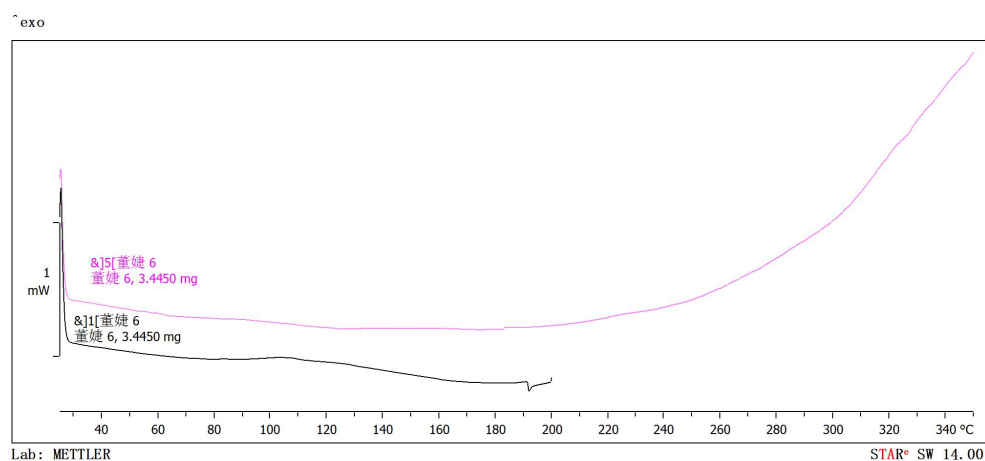


Figure S58. DSC thermograms of NB-UA copolymer obtained by Table 2 entry 15.

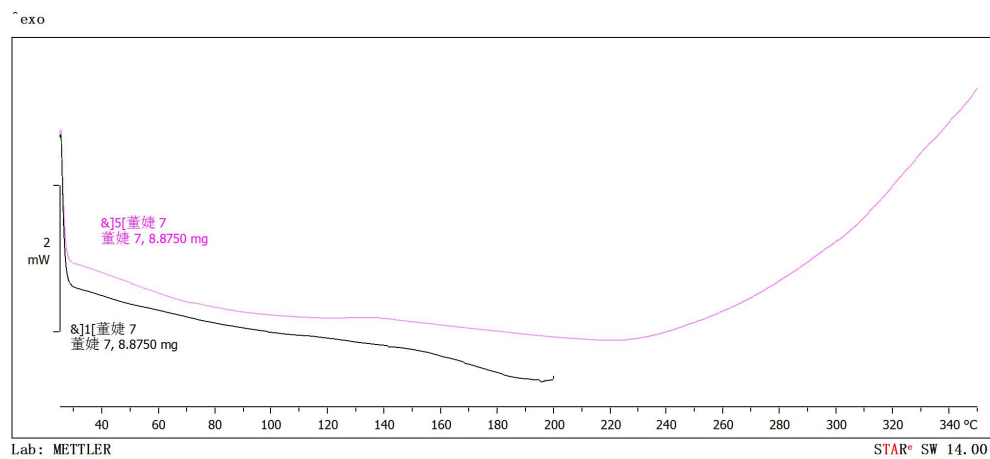


Figure S59. DSC thermograms of NB-UA copolymer obtained by Table 2 entry 16.

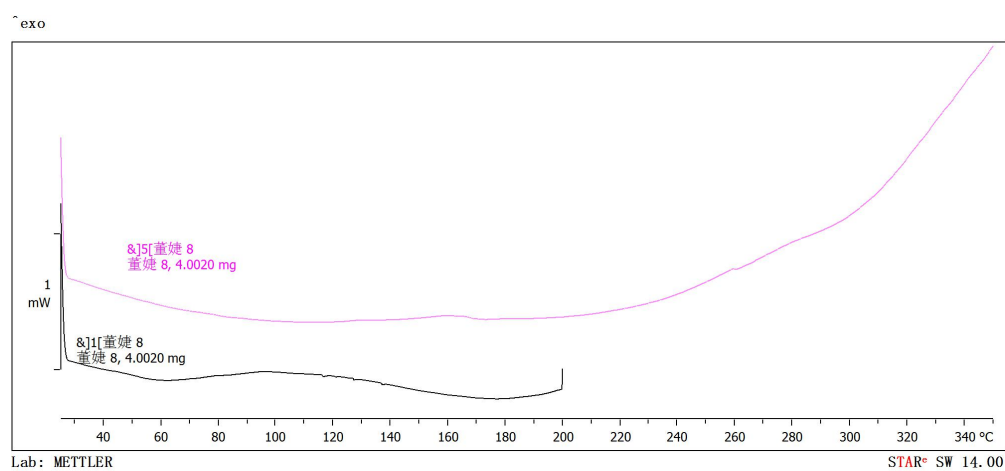


Figure S60. DSC thermograms of NB-UA copolymer obtained by Table 2 entry 17.

7. X-ray crystallography of complexes 3, 4a, and 4b

Complex	[3-3]·CH ₂ Cl ₂	4a	4b·0.13 CH ₂ Cl ₂
Empirical formula	C ₃₇ H ₅₄ Cl ₄ N ₆ O ₂ Pd ₂	C ₃₂ H ₃₄ ClN ₃ OPd	C _{34.13} H _{38.25} Cl _{1.25} N ₃ O ₃ Pd
Formula weight	969.46	618.47	689.14
Temperature	113.15 K	113(2) K	113.15 K
Crystal system	triclinic	Monoclinic	monoclinic
space group	P-1	P2(1)/n	I2/a
Unit cell dimensions	a = 9.5481(5) Å b = 15.1927(7) Å c = 15.9838(8) Å α = 62.136(5) ° β = 84.247(4) ° γ = 84.451(4) °	a = 13.427(3) Å b = 10.938(2) Å c = 19.798(4) Å α = 90 ° β = 107.14(3) ° γ = 90 °	18.1028(7) Å 14.4854(5) Å 24.8028(9) Å α = 90 ° β = 101.780(4) ° γ = 90 °
Volume	2036.21(19) Å ³	2778.5(11) Å ³	6367.0(4) Å ³
Z	2	4	8
Calculated density	1.581 g/cm ³	1.478 g/cm ³	1.438 g/cm ³
Absorption coefficient	1.186 mm ⁻¹	0.794 mm ⁻¹	0.726 mm ⁻¹
F(000)	988.0	1272	2842.0
Crystal size	0.2 x 0.18 x 0.16 mm ³	0.200 x 0.180 x 0.120 mm ³	0.19 x 0.17 x 0.15 mm ³
2θ range for data collection	4.988 to 52.744 °	1.634 to 27.879 °	3.354 to 52.734 °
Index ranges	-11 ≤ h ≤ 11,	-17 ≤ h ≤ 17,	-22 ≤ h ≤ 22,
Reflections collected	21597	32586	33438
Independent reflections	8298 [R(int) = 0.0574, R(sigma) = 0.0681]	6620 [R(int) = 0.0548]	6509 [R(int) = 0.0692, R(sigma) = 0.0513]
Data / restraints / parameters	8298/0/472	6620 / 6 / 349	6509/21/414
Goodness-of-fit on F ²	1.064	1.081	1.043
Final R indices [I ≥ 2σ (I)]	R1 = 0.0392, wR2 = 0.0816	R1 = 0.0375, wR2 = 0.0863	R1 = 0.0402, wR2 = 0.0822
R indices (all data)	R1 = 0.0524, wR2 = 0.0916	R1 = 0.0446, wR2 = 0.0908	R1 = 0.0544, wR2 = 0.0900
Largest diff. peak and hole	0.68/-0.93 e Å ⁻³	1.204/-0.963 e Å ⁻³	0.57/-0.53 e Å ⁻³